FISHERIES RESEARCH BOARD OF CANADA

(FORMERLY BIOLOGICAL BOARD OF CANADA)

UNDER THE CONTROL OF

THE HON. THE MINISTER OF FISHERIES

BULLETIN No. LIX

THE CHEMISTRY AND TECHNOLOGY OF MARINE ANIMAL OILS WITH PARTICULAR REFERENCE TO THOSE OF CANADA

EDITED BY

H. N. BROCKLESBY

(Foreword by J. Dybhavn)

FOREWORD

Since the publication of Bulletin XXXVII in 1933 work on various phases of the chemistry and utilization of marine animal oils has been carried on and notable progress made.

In view of this the Fisheries Research Board of Canada is now making available to the industry and other interested parties a similar Bulletin that summarizes our knowledge of marine animal oils up to the end of 1939 and that includes data on the oils of both coasts of Canada.

To gather all these facts and properly assemble them for publication has taken longer than originally planned, but as a result it is felt that a most useful Bulletin is now being presented and it is our sincere hope that it will prove of valuable interest and assistance to our industries.

JOHN DYBHAVN,
Chairman, Pacific Sub-Executive Committee,
Fisheries Research Board of Canada

Prince Rupert, B.C.
July, 1940.

PREFACE

In 1932 the editor of this Bulletin and Dr. O. F. Denstedt, then of the staff of the Pacific Fisheries Experimental Station, were instructed by the Biological Board of Canada to gather information available concerning the chemistry and technology of marine animal oils and, together with the data obtained in researches carried out at this Station, to publish the material in a form that would be acceptable to the industry of Canada. In spite of many shortcomings the Bulletin that was prepared proved to be of definite value to the fishing industry and to users of marine animal oils. As with all monographs of this nature, the first edition was soon out of date and the need for a revised edition was soon apparent.

From our experience with the reception and comments on that Bulletin, plus a consideration of the diverse nature of the numerous requests for information regarding marine animal oils received at this Station, the conception of the present one has gradually evolved. It is more ambitious in its scope; the range of subjects dealt with has been chosen largely with the view of presenting logical answers to questions asked of this Station during the past seven years. If there are criticisms regarding the subject matter and amount of space devoted to the various phases of the chemistry and technology of marine animal oils, the editor can only plead that the effort was directed mainly along those lines in which greatest interest was taken by the particular industries concerned.

This Bulletin reviews the literature up to the end of 1939 and in addition contains considerable original work not hitherto published. In view of the varied nature of the audience to whom it is addressed it was once again considered advisable to include some elementary chemistry. As with the other, this Bulletin is intended for research and industrial chemists, production managers, plant foremen, sales engineers, oil brokers and perhaps an executive or two. It will therefore be realized that a single style of presentation for every subject dealt with is not possible, even though it were desirable. The writers of the various sections have had in mind the requirements of the reader to whom his particular subject has the most interest, but it is to be hoped that the whole will be found to be a logical development of a subject of some technical and economic interest to Canada.

It is intended to publish a supplementary Bulletin dealing with methods and interpretations of analyses, with particular reference to those that have been used at this Station and found satisfactory for the examination of marine animal oils.

The editor wishes sincerely to thank Miss Norma Rogers for invaluable assistance in the general preparation of the manuscript, Mr. Lyle A. Swain for editorial assistance and Dr. N. M. Carter for much assistance and advice in the planning of the Bulletin.

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The whole-hearted support of the industry is also to be acknowledged. In particular the following firms should be especially mentioned for supplying information and illustrations of equipment: F. E. Booth Co., San Francisco, Calif.; The B.C. Packers Ltd., Vancouver, B.C.; The J. H. Carson Co., Prince Rupert, B.C.; The California Press Manufacturing Co., San Francisco, Calif.; The Canadian Fishing Co., Vancouver, B.C.; The DeLaval Pacific Co., San Francisco, Calif.; Wm. Garrigue and Co. Inc., Chicago, Ill.; Rose Downs Thompson, Ltd., Hull, Eng.; Ernest Scott and Co., Ltd., London, Eng.; The Sharples Specialty Co., San Francisco, Calif.; Technical Research Works, London, Eng.; The Titan Co., Copenhagen, Denmark, and Wurster and Sanger Inc., Chicago, Ill.

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SECTION 1. GENERAL CHEMISTRY OF MARINE ANIMAL OILS AND FATS

In this Bulletin it is necessary to use numerous chemical and other terms which may possibly be unfamiliar to non-chemists. A number of these are therefore now defined.

I. GENERAL DEFINITIONS

Marine animal oils and fats are not chemically homogeneous materials in the natural state. Each is a mixture of many organic chemical substances, consisting chiefly of various liquid or solid representatives of the one class of chemical compounds that constitutes all pure *fats* and *fatty oils*. Unfortunately the word *oil* is applied to both the true fatty oils and to at least two other groups of quite unrelated chemical substances, the petroleum (paraffin) oils and the non-drying essential (aromatic) oils. Fatty oils are merely *fats* that happen to be liquid at ordinary temperatures. In industrial practice the distinction between an oil and a fat is usually made by considering their physical condition at a temperature of about 60°F., hence marine animal fats and oils may be considered as synonymous terms for most purposes.

Stearine is an alternate, general term for the solid or semi-solid fats that separate from a fatty oil upon cooling. Since as mentioned above marine animal oils consist of mixtures of many individual fatty oils, the process of stearine separation takes place in stages during cooling. The amount of stearine that separates at any given temperature will depend on the melting points of the fats constituting the oil. Some oils, such as raw herring oil, will contain an appreciable amount of stearine at temperatures well above 60°F., while other raw oils, such as porpoise jaw oil, will not deposit stearine until the temperature has fallen considerably below 60°F. Since the term stearine will be extensively used throughout this Bulletin, it is desirable to emphasize that it must not be confused with the word *stearin* that denotes one particular, chemically homogeneous fat. Stearin itself may be one of the constituents of the stearine separating from certain fish oils upon cooling.

Certain other substances found in marine animal oils and fats, though not necessarily chemically related to the fats, are the *pigments*, *sterols*, *vitamins*, *ethers*, *waxes* and *hydrocarbons*. These substances, present in the oils by virtue of their oil-soluble properties, are grouped collectively as the *non-saponifiable* components of fish oils since they form the inert residue in the manufacture of soaps from such oils. Small amounts of organic *fatty acids* and *glycerol*, resulting from incipient breakdown of fats, may also be present in an oil.

There is looseness in the industrial use of the word *wax*. The oil from the head cavities of the sperm whale contains a large proportion of a true wax, known as spermaceti, dissolved in the oil; paraffin "wax" is actually a solid representative

of the class of chemical compounds to which mineral oils belong, and Japan "wax" is really a fat. The hydrocarbons found in some fish oils, such as the squalene in dogfish liver oil, are chemically much more closely related to the mineral oils than to the fatty oils.

II. CHEMICAL DEFINITIONS

True fatty oils are composed exclusively of *atoms* of three chemical *elements*, carbon, hydrogen and oxygen. Single atoms of these elements are designated respectively by the capital letters C, H and O. Non-saponifiable components dissolved in the oils may be composed of carbon and hydrogen alone (hydrocarbons), or carbon and hydrogen together with oxygen and additional elements such as nitrogen (N), phosphorus (P) and sulphur (S). Individual atoms seldom exist by themselves, but tend to combine with other atoms of the same element or with atoms of different elements. The resultant combinations are known as *molecules*. When the union is between two or more atoms of the same element, the product is a *molecule* of the *element* (*e.g.* two atoms of hydrogen, H+H, give a molecule of hydrogen, designated by H_2). When the union is between two or more atoms of different elements, the product is a *molecule* of a *chemical compound* (*e.g.* two atoms of hydrogen and one atom of oxygen, H+H+O, give a molecule of water, designated by H_2O). This tendency of atoms to unite with one another to form molecules is a result of their mutual *chemical affinities*, which may be very great, as between the two hydrogen atoms and one oxygen atom that unite explosively to form a molecule of water, or may be very slight, as evidenced by the disinclination of atoms of the element neon (Ne) to unite either with themselves or with atoms of other elements.

The chemical affinity of an atom can be considered as being concentrated at one or more "centres of attraction" for other atoms. The number of these centres in any one atom determines what is known as the *valency* of that atom or element. The atoms of a given element usually have a characteristic valency, which may be any number from zero to eight, though the atoms of some elements may exhibit different valencies in different molecules. Most of the elements comprising the substances discussed in this Bulletin have a valency not exceeding four. The forces exerted by these centres of chemical affinity can be likened in a sense to "arms" reaching out to link with the arms of other atoms, the number of arms being equal to the valency. An atom of hydrogen invariably has only one centre of attraction or arm, which may be represented by H–, indicating a valency of one, or *monovalency*. An oxygen atom is *divalent* and is represented by –O– or O =. An example of a *trivalent* atom is that of nitrogen (–N=) although it can also have a valency of five. Carbon atoms are *tetravalent* and for graphical purposes are variously represented thus:

$$-\overset{|}{\underset{|}{C}}- \qquad =C= \qquad \overset{|}{\underset{|}{C}}= \qquad -C\equiv$$

Generally speaking, when atoms of two different elements unite, their valencies must be mutually satisfied. Thus a monovalent atom may unite with one other like or unlike monovalent atom (H– + –H to give H–H or H_2); a divalent atom may unite with two monovalent atom (H– + –O– + –H to give H–O–H or H_2O), with one like or unlike divalent atom as in O = O (oxygen, O_2) and Ca = O (calcium oxide or quicklime, CaO), or with two like or unlike atoms of valency two or more, as in the following molecules:

$$\underset{O\;-\;O}{\overset{O}{\diagup\diagdown}} \text{(ozone, } O_3\text{)}, \qquad \underset{>C\;-\;C<}{\overset{O}{\diagup\diagdown}} \quad \text{and} \quad \underset{N\;=\;N}{\overset{O}{\diagup\diagdown}} \text{(nitrous oxide, } N_2O\text{)}.$$
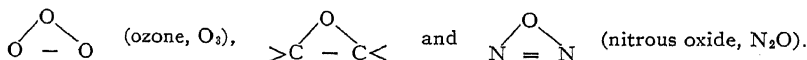
A tetravalent atom such as carbon may form various molecular combinations such as

$$\overset{H}{\underset{H}{\overset{|}{H-C-H}}} \qquad O=C=O \qquad \overset{H}{\overset{|}{H-C=O}} \qquad \overset{H\ \ H}{\underset{H\ \ H}{\overset{|\ \ |}{H-C-C-H}}} \qquad \overset{H\ \ \ H}{\underset{H\ \ \ H}{\overset{|\ \ \ |}{C=C}}} \qquad \overset{H\ \ \ H}{\overset{|\ \ \ |}{C\equiv C}}$$

| Methane, or marsh gas, CH_4 | Carbon dioxide, CO_2 | Formaldehyde, CH_2O | Ethane, C_2H_6 | Ethylene, C_2H_4 | Acetylene, C_2H_2 |

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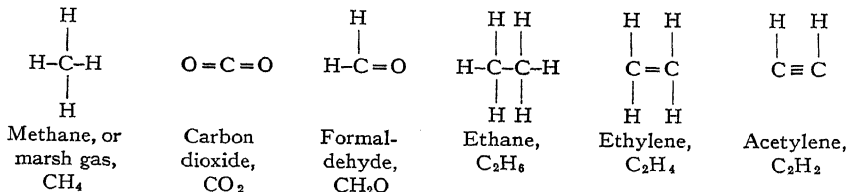
It is essential to note that *all* the normal valency arms of an atom must be satisfied by linking with the requisite number of valency arms of the adjoining atoms. The foregoing examples illustrate two methods of writing a *chemical formula*. When the linking of the valency arms is designated by dashes or *bonds* between the atoms, the resulting representation of the structure of the molecule is termed a *graphical formula*, although the actual relative positions of the atoms are not necessarily as shown. The shorter expression below the name of each compound is called its *condensed formula*. The number of valency bonds separating atoms or groups of atoms is often represented by dots instead of dashes, as O:C:O for CO_2; $H.CH_3$ for CH_4.

The formula for ethane above illustrates one important characteristic of carbon atoms that has a great significance in the chemistry of marine animal oils. One of the valencies of a carbon atom may form a *single bond* with one of the valencies of an adjoining carbon atom, and the process may be continued thus:

$$
\begin{array}{ccccc}
H & H & H & H & H \\
| & | & | & | & | \\
H-C-&C-&C-&C-&C- \\
| & | & | & | & | \\
H & H & H & H & H \\
\end{array}
$$ until as many as sixty or more carbon atoms are linked together to form what
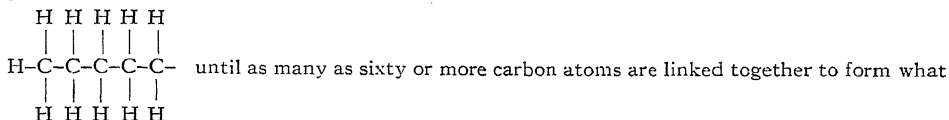
is known as a *carbon atom chain*. Actually the chains are not straight, but tend to assume a zig-zag configuration. There also exist *branched carbon atom chains* and *carbon atom rings* of various sizes, but these are rarely if ever encountered in naturally occurring marine animal oils though they may be formed during certain treatments of such oils.

The incomplete chain of five carbon atoms illustrated by the last formula has one remaining unoccupied valence arm and as such does not represent an actual chemical compound, but is known as an *organic radical*. The condensed formula for the example shown is variously written as $CH_3.CH_2.CH_2.CH_2.CH_2-$, $C_5H_{11}-$, $C_nH_{2n+1}-$ where $n=5$, $CH_3(CH_2)_4-$, or $CH_3(CH_2)_n-$ where $n=4$. The formula for an organic radical is often abbreviated to the letter R. If the unoccupied valence arm of the generalized radical $C_nH_{2n+1}-$ is satisfied by a terminal monovalent atom or group of atoms, the resulting actual chemical compounds (*e.g.*, $C_nH_{2n+1}-H$, the hydrocarbons) have physical and chemical properties depending on the value of *n*. By giving *n* successive values of 1, 2, 3, 4, etc., the compounds represented by the resulting formulae will exhibit definite gradations in physical and chemical properties and are said to form a *homologous series*. Thus, there are homologous series of hydrocarbons, fatty acids, fatty alcohols, etc. The physical property of "fattiness" or "oiliness" does not become evident in these acids and alcohols until *n* has a value of 8 or more. Expressions such as "C_{16} acid" or "C_{18} alcohol" frequently used in this Bulletin indicate the *total number of carbon atoms* in the chain comprising the molecule of the compound. This is a convenient way of referring to a fatty acid or alcohol that has no simple name; their systematic names are mentioned later.

Of the many classes of chemical compounds into which a carbon atom chain enters as a radical, only a few have a direct bearing on the chemical constitution of marine animal oils. These are now briefly described.

(a) CARBON ATOM CHAINS AND DERIVATIVES

Hydrocarbons are formed when the carbon atom chain is combined with hydrogen atoms only (*e.g.*, methane, ethane, ethylene and acetylene shown by the formulae on page 14). The typical formula is R–H. Only a few hydrocarbons, all of which have long carbon chains, have been recognized in marine animal oils.

Fatty acids are characterized by the carbon atom chain being terminated by the atomic group $-C\!\!\begin{array}{c} \nearrow O \\ \searrow O-H \end{array}$, known as the *carboxyl group* and usually abbreviated to –COOH. The typical formula of a fatty acid is therefore R–COOH. One important property of fatty acids is the ease with which the hydrogen atom of the carboxyl group reacts with other groups (page 18) and can be replaced by metals to form *soaps* (page 29). The great variations in the properties of fats and oils are principally due to the diversity of the fatty acids which, in chemical combination as

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described later, form the chief constituent of fat and fatty oil molecules. This diversity of fatty acids is illustrated by the following types.

Saturated fatty acids have all carbon atoms linked with each other by single bonds only:

H–C–C–C–C–C–C–C–COOH (with H atoms above and below each carbon)
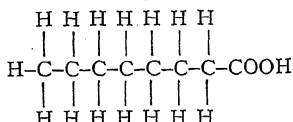
Condensed formula, $C_8H_{16}O_2$ or
$C_nH_{2n}O_2$ where $n=8$,
$C_nH_{2n+1}.COOH$ where $n=7$.

With one or two exceptions, only fatty acids having an *even* number of carbon atoms are found in natural products, including marine animals oils. Therefore n is *even* when the general formulae $C_nH_{2n}O_2$ and $CH_3(CH_2)_n.COOH$ are used in representing such acids, but is *odd* when the general formula $C_nH_{2n+1}.COOH$ is used. (See formulae in tables II and III).

Unsaturated fatty acids have some of the carbon atoms linked with each other by double bonds:

H–C–C–C=C–C–C–C–COOH
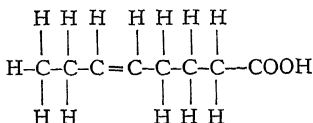
Condensed formula, $C_8H_{14}O_2$ or
$C_nH_{2n-2}O_2$ where $n=8$,
$C_nH_{2n-1}.COOH$ where $n=7$.

The resulting $C=C$ linkage is the same as that in the formula given for ethylene (page 14) and is variously called a *double bond, unsaturated bond, ethenoid bond, ethylene bond,* or *ethylenic bond.* Unsaturated fatty acids may have one, two and three, and sometimes six or more such double bonds per molecule and the position of the bonds along the carbon chain may vary. In the group here shown for comparison,

$CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-(CH_2)_7-COOH$ or $C_{18}H_{36}O_2$ (a)
$CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH=CH-(CH_2)_7-COOH$ or $C_{18}H_{34}O_2$ (b)
$CH_3-CH_2-CH_2-CH_2-CH_2-CH=CH-CH_2-CH=CH-(CH_2)_7-COOH$ or $C_{18}H_{32}O_2$ (c)
$CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH=CH-CH=CH-(CH_2)_7-COOH$ or $C_{18}H_{32}O_2$ (d)
$CH_3-CH_2-CH=CH-CH_2-CH=CH-CH_2-CH=CH-(CH_2)_7-COOH$ or $C_{18}H_{30}O_2$ (e)

acids "a" (stearic), "b" (oleic), "c" (linolic) and "e" (linolenic), having respectively 0, 1, 2 and 3 double bonds, are representative *saturated, mono-unsaturated, di-unsaturated* and *tri-unsaturated* fatty acids. Acid "d" has the same condensed formula as acid "c" but differs in having one of its two double bonds in a different position in the chain. This is an example of a type of *isomerism,* a term described more fully on page 20. If the carbon atoms are numbered commencing with that of the carboxyl group as 1, the position of the double bonds may be designated by indicating the two carbon atoms joined by a double bond. For example, acid "c" is 9:10, 12:13-linolic acid; acid "d" is 9:10, 11:12-linolic acid. Frequently only the first numeral of each pair is given, as 9, 12-linolic acid for 9:10, 12:13-linolic acid. A systematic nomenclature is also available in which prefixes designate the total number of carbon atoms in a chain, a vowel change differentiates saturated from unsaturated chains, an adjective indicates the presence of two or more double bonds, and a suffix denotes the chemical nature of the compound. Acids are designated by the suffix "-oic" (octadeca = 18 di = 2; tri = 3; etc.):

Stearic   acid —   octadec-an-oic   acid
Oleic   acid —   9-octadec-en-oic   acid
Linolic   acid —   9, 12-octadeca-di-en-oic acid
Linolenic acid — 9, 12, 15-octadeca-tri-en-oic acid

In actual practice, the hyphens between the syllables are omitted. Tables II and III illustrate the nomenclature of the even-numbered fatty acids. The same system of nomenclature serves for alcohols (suffix "-ol"), aldehydes (suffix "-al"), etc.

Unsaturated fatty acids have a marked chemical affinity for certain elements and compounds. This affinity is centred in the double bond, which is not to be interpreted as a union of twice the

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strength of a single bond, but rather as the combination of one normal linkage and one "temporary" linkage that may readily be opened to re-form one free valency arm on each of the carbon atoms concerned, ready to unite with other substances available. In the presence of chlorine (Cl), bromine (Br) and iodine (I) the opening of the bond and union with the element takes place readily; under the influence of heat and pressure or in the presence of a *catalyst* (promotor), hydrogen can be added to the double bond by a process known as *hydrogenation* to produce a saturated bond; oxygen from the atmosphere will combine with double bonds to produce the phenomenon known ᵢ *drying* of the oils; and other substances such as sulphur, sulphuric acid, water, etc., react more or lᵤ₋₋ dily as described in later sections. The double bond (or bonds) of one acid can open to unite with tnosᵗ of other unsaturated acids, thus forming a cross-linkage between the acids in the form of carbon atoₘᵢ ring:

$$R–CH=CH–(CH_2)_n.COOH \qquad\qquad R–CH–CH–(CH_2)_n.COOH$$
$$\longrightarrow$$
$$HOOC.(CH_2)_n–CH=CH–R \qquad\qquad HOOC.(CH_2)_n–CH–CH–R$$
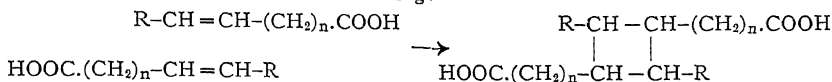
This formation of rings is very probably one of the factors contributing to the remarkable changes in physical properties that take place in an unsaturated fish oil when it is subjected to certain heat treatments and other processes discussed in Section 5 I(d). The special arrangement –CH=CH–CH=CH– of the double bonds in acid "d" of the foregoing comparison group is one that does not normally occur in marine animal oils, but it can be produced by self-rearrangement of otherwise distributed double bonds when such oils or their fatty acids are heated in the presence of catalysts or other chemical agents. The *conjugated double bonds* so produced do not react as two double bonds, but rather as a special single unit of unsaturation. For example, in the chlorination of a fatty acid containing a conjugated double bond, only two atoms of chlorine would be combined instead of four as expected, and a new double bond of different properties appears where the central single bond formerly existed:

$$-CH=CH–CH=CH– \qquad\qquad -CH–CH=CH–CH–$$
$$Cl–Cl \qquad\qquad\qquad \longrightarrow \qquad\qquad Cl \qquad\qquad Cl$$

Alcohols are characterized by the groupings

H	R	R
R–C–O–H	H–C–O–H	R–C–O–H
H	R	R
Primary alcohol,	Secondary alcohol,	Tertiary alcohol,
$R.CH_2OH$	$RR.CHOH$	$RRR.COH$
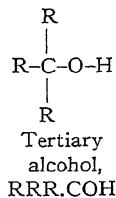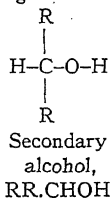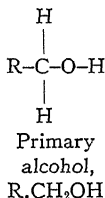
The term "fatty alcohols" is understood to mean primary alcohols having eight or more carbon atoms in the chain.

There may be more than one alcoholic group per molecule, as exemplified by the most important alcohol in the chemistry of oils, namely *glycerol* (glycerin, glycerine). Glycerol has the

formula
$$CH_2OH$$
$$|$$
$$CH.OH$$
$$|$$
$$CH_2OH$$
and is thus a chain of three carbon atoms to which are attached *three*
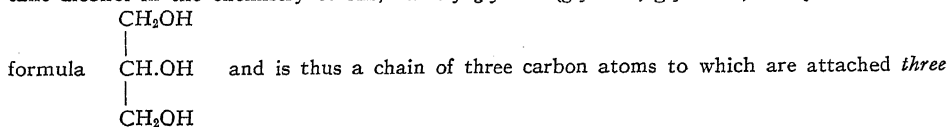
alcoholic groups, one primary group at each end and a secondary group in the centre.

The –OH part of alcoholic groups is termed *hydroxyl* and exhibits a marked tendency to combine with the hydrogen of the carboxyl group (–COOH) of fatty acids. (See *esters* below.)

Aldehydes are characterized by the grouping $-C\begin{smallmatrix}\diagup O \\ \diagdown H\end{smallmatrix}$ (usually abbreviated to –CHO), known

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as the *aldehyde group*. Aldehydes are not usually found in fats, but may be produced when rancidity occurs (page 178).

$$O$$
$$\|$$

Ketones are characterized by the grouping $C-C-C$ and like aldehydes, are not usually found in fats but are produced therefrom during development of certain types of rancidity.

(b) COMPOUNDS RESULTING FROM UNION OF CARBON CHAIN DERIVATIVES

Esters represent by far the most important type of compound present in fish (and marine animal) fats and oils since all pure fats, fatty oils and true waxes are esters. They result from the chemical union of fatty acids with alcohols:

$$R-CH_2-OH \quad + \quad H-O-CO-R \quad \longrightarrow \quad R-CH_2-O-CO-R \quad + \quad H-O-H$$

     Alcohol   Fatty acid   Ester   Water
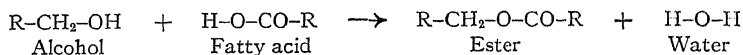
The hydroxyl (–OH) of the alcoholic group unites with the reactive hydrogen (H–) of the carboxyl group of the acid to form water, leaving the remainders ($R-CH_2-$ and $-O-CO-R$) of the alcohol and acid molecules united to form the ester. The *methyl esters of fatty acids* used in the separation and the identification of fatty acids from fats are thus prepared:

$$C_{17}H_{33}COOH \quad + \quad CH_3OH \quad \longrightarrow \quad C_{17}H_{33}COOCH_3 \quad + \quad H_2O$$

   Oleic acid   Methyl alcohol   Methyl oleate   Water
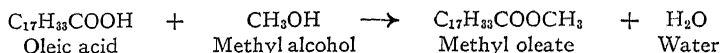
The number of alcoholic groups per molecule of alcohol determines how many molecules of fatty acids can combine with that alcohol molecule. When alcohols containing only *one* alcoholic group unite with a molecule of a fatty acid the resultant esters such as the above two examples are termed *mono-esters*, and when certain complex alcohols and acids are involved, special mono-esters called *waxes* result; *e.g.*, $CH_3(CH_2)_{12}COO(CH_2)_{15}CH_3$, cetyl myristate, a wax found in spermaceti. When the alcohol glycerol, containing *three* alcoholic groups, combines with fatty acids, the resulting *tri-esters* are termed *glycerides*, a general name for *fats* and *fatty oils*:

$$CH_2-OH \quad + \quad H-O-CO-(CH_2)_nCH_3 \qquad CH_2-O-CO-(CH_2)_nCH_3$$
$$|\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad |$$
$$CH-OH \quad + \quad H-O-CO-(CH_2)_nCH_3 \longrightarrow CH-O-CO-(CH_2)_nCH_3 \quad + \quad 3H_2O$$
$$|\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad |$$
$$CH_2-OH \quad + \quad H-O-CO-(CH_2)_nCH_3 \qquad CH_2-O-CO-(CH_2)_nCH_3$$

One molecule   Three molecules   One molecule of   Three
of glycerol   of fatty acids   ester, a fat   molecules of
                                                                 water
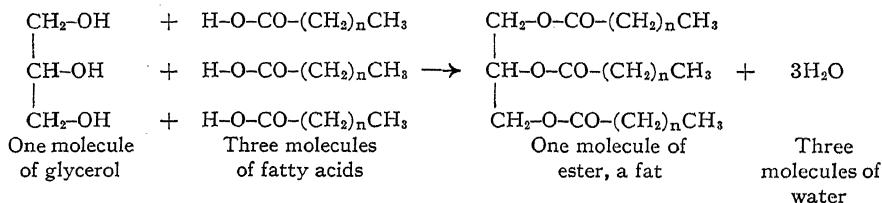
The three molecules of fatty acids may be identical or different, and "n" in natural fats may have any even value up to 30 [with one or two exceptions as in the case of the isovaleric acid ($n = 3$) obtained from porpoise jaw oil].

     The immense variety of glycerides that may be found in fats and oils is evident from a consideration of the numerous possible combinations between glycerol and the acid groups $-O.CO.R_1$, $-O.CO.R_2$ and $-O.CO.R_3$ of three different fatty acids, as shown in figure 1. (R_1, R_2 and R_3 represent carbon atom chains of different lengths.) Each of the glycerides represented in figure 1 has its own peculiar properties such as a specific melting point, solubility, etc. Formulae connected by underlining represent glycerides of the same composition but different properties, a phenomenon discussed under structural isomerism on page 20. It is therefore evident that the number of different glycerides obtainable from relatively few fatty acids is very great.

In natural fats and oils, the existence of monoglycerides and diglycerides is doubtful and simple triglycerides are probably uncommon. By far the larger number of glycerides present belong to the mixed triglyceride type.

MONOGLYCERIDES

$$
\begin{array}{llll}
CH_2O.CO.R_1 & CH_2OH & CH_2O.CO.R_2 & CH_2OH \\
CHOH & CHO.CO.R_1 & CHOH & CHO.CO.R_2 \\
CH_2OH & CH_2OH & CH_2OH & CH_2OH
\end{array}
\qquad
\begin{array}{ll}
CH_2O.CO.R_3 & CH_2OH \\
CHOH & CHO.CO.R_3 \\
CH_2OH & CH_2OH
\end{array}
$$

SIMPLE   DIGLYCERIDES

$$
\begin{array}{llll}
CH_2O.CO.R_1 & CH_2O.CO.R_1 & CH_2O.CO.R_2 & CH_2O.CO.R_2 \\
CHO.CO.R_1 & CHOH & CHO.CO.R_2 & CHOH \\
CH_2OH & CH_2O.CO.R_1 & CH_2OH & CH_2O.CO.R_2
\end{array}
\qquad
\begin{array}{ll}
CH_2O.CO.R_3 & CH_2O.CO.R_3 \\
CHO.CO.R_3 & CHOH \\
CH_2OH & CH_2O.CO.R_3
\end{array}
$$

MIXED   DIGLYCERIDES

$$
\begin{array}{llll}
CH_2O.CO.R_1 & CH_2O.CO.R_1 & CH_2O.CO.R_1 & CH_2O.CO.R_1 \\
CHO.CO.R_2 & CHOH & CHO.CO.R_3 & CHOH \\
CH_2OH & CH_2O.CO.R_2 & CH_2OH & CH_2O.CO.R_3
\end{array}
\qquad
\begin{array}{ll}
CH_2O.CO.R_2 & CH_2O.CO.R_2 \\
CHO.CO.R_3 & CHOH \\
CH_2OH & CH_2O.CO.R_3
\end{array}
$$

$$
\begin{array}{lll}
CH_2O.CO.R_2 & CH_2O.CO.R_3 & CH_2O.CO.R_3 \\
CHO.CO.R_1 & CHO.CO.R_1 & CHO.CO.R_2 \\
CH_2OH & CH_2OH & CH_2OH
\end{array}
$$

SIMPLE   TRIGLYCERIDES

$$
\begin{array}{lll}
CH_2O.CO.R_1 & CH_2O.CO.R_2 & CH_2O.CO.R_3 \\
CHO.CO.R_1 & CHO.CO.R_2 & CHO.CO.R_3 \\
CH_2O.CO.R_1 & CH_2O.CO.R_2 & CH_2O.CO.R_3
\end{array}
$$

MIXED   TRIGLYCERIDES

$$
\begin{array}{llll}
CH_2O.CO.R_1 & CH_2O.CO.R_1 & CH_2O.CO.R_2 & CH_2O.CO.R_2 \\
CHO.CO.R_1 & CHO.CO.R_2 & CHO.CO.R_2 & CHO.CO.R_1 \\
CH_2O.CO.R_2 & CH_2O.CO.R_1 & CH_2O.CO.R_1 & CH_2O.CO.R_2
\end{array}
\qquad
\begin{array}{ll}
CH_2O.CO.R_3 & CH_2O.CO.R_3 \\
CHO.CO.R_3 & CHO.CO.R_1 \\
CH_2O.CO.R_1 & CH_2O.CO.R_3
\end{array}
$$

$$
\begin{array}{llll}
CH_2O.CO.R_1 & CH_2O.CO.R_1 & CH_2O.CO.R_2 & CH_2O.CO.R_2 \\
CHO.CO.R_1 & CHO.CO.R_3 & CHO.CO.R_2 & CHO.CO.R_3 \\
CH_2O.CO.R_3 & CH_2O.CO.R_1 & CH_2O.CO.R_3 & CH_2O.CO.R_2
\end{array}
\qquad
\begin{array}{ll}
CH_2O.CO.R_3 & CH_2O.CO.R_3 \\
CHO.CO.R_3 & CHO.CO.R_2 \\
CH_2O.CO.R_2 & CH_2O.CO.R_3
\end{array}
$$

$$
\begin{array}{lll}
CH_2O.CO.R_1 & CH_2O.CO.R_1 & CH_2O.CO.R_3 \\
CHO.CO.R_3 & CHO.CO.R_2 & CHO.CO.R_1 \\
CH_2O.CO.R_2 & CH_2O.CO.R_3 & CH_2O.CO.R_2
\end{array}
$$

FIGURE 1. Possible monoglycerides, diglycerides, and triglycerides (fats) resulting from the union of glycerol with three different fatty acids. Compounds represented by formulae connected by underlining are isomeric.

Another type of ester that does not properly fall in the class being discussed may well be defined here. Besides combining with fatty acids, alcohols may combine with *inorganic acids* (acids that contain neither carbon nor the carboxyl group, but exhibit the readily replaceable hydrogen characteristic of all acids) to form *inorganic esters*. Those of the well-known acids hydrochloric (muriatic, HCl), sulphuric $\left(\begin{array}{l}H-O \\ H-O\end{array}\!\!>SO_2,\ H-O-SO_3H\ \text{or}\ H_2SO_4\right)$, and phosphoric

$$\left(\begin{array}{c} H\text{-}O \\ H\text{-}O \\ H\text{-}O \end{array}\!\!\!\!\!\!\searrow\!\!P = O \text{ or } H_3PO_4 \right)$$ are examples of this class. Only a few inorganic esters come under consideration in this Bulletin, the chief being certain lipoids found in the unsaponifiable matter, and the manufactured sulphated oils:

$$\begin{array}{ll}
CH_2\text{-}O\text{-}CO\text{-}R & \qquad CH_2\text{-}O\text{-}CO\text{-}R \\
\quad | & \qquad\quad | \\
CH\text{-}O\text{-}CO\text{-}R & \qquad CH\text{-}O\text{-}CO\text{-}R \\
\quad | & \qquad\quad | \\
CH_2\text{-}O\text{-}P\text{-}OH & \qquad CH_2\text{-}O\text{-}SO_3H \\
\quad\ \ \diagup\!\!\diagdown & \\
\quad O\quad OH &
\end{array}$$
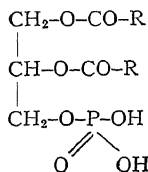
<table>
<tr><td style="text-align:center">Mixed phosphoric and fatty acid
ester of glycerol, the parent sub-
stance of the phospholipoids.</td><td style="text-align:center">Mixed sulphuric and fatty acid
ester of glycerol, or one type of
sulphated oil.</td></tr>
</table>
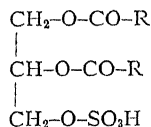
Ethers result from chemical combination between two alcohol molecules with the simultaneous splitting off of one molecule of water formed,

$$\begin{array}{cccccc}
R\text{-}CH_2\text{-}OH & + & H\text{-}O\text{-}CH_2\text{-}R & \longrightarrow & R\text{-}CH_2\text{-}O\text{-}CH_2\text{-}R & + & H\text{-}O\text{-}H \\
\text{Alcohol} & & \text{Alcohol} & & \text{Ether} & & \text{Water}
\end{array}$$
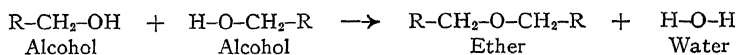
and are found in the unsaponifiable portion of fish oils as mono-ethers of glycerol, $\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2\text{-}O\text{-}R \end{array}$. Because there are two alcohol groups to one ether linkage in such molecules, these compounds received names such as chimyl alcohol ($R = C_{16}H_{33}$), batyl alcohol ($R = C_{18}H_{37}$) and selachyl alcohol ($R = C_{18}H_{35}$). They exist in the oils as diglycerides $\begin{array}{l} CH_2O\text{-}CO\text{-}R_1 \\ | \\ CHO\text{-}CO\text{-}R_2 \\ | \\ CH_2\text{-}O\text{-}R \end{array}$ but the two fatty acid portions ($-CO\text{-}R_1$ and $-CO\text{-}R_2$) are broken off during the saponification.

III. ISOMERISM

Compounds are said to exhibit isomerism, or to be *isomeric*, when they are composed of the same proportions of the same elements (i.e. have identical condensed formulae) but exhibit different chemical or physical properties. Isomerism may be of two kinds: (*a*) structural, (*b*) spatial. The latter is divided into two types, geometrical and optical. Although optical isomerism can exist in fish fats, it has little bearing on their industrial utilization.

(*a*) STRUCTURAL ISOMERISM

Structural isomerism arises through differences in the order in which the same groups of atoms are arranged in a molecule, as illustrated by the four arrangements for $CH_3.CH_2.CH_2CH_2.COOH$ (valeric acid):

H | $CH_3.CH_2.CH_2–C–COOH$ | H	CH_3 H |————| $CH_3–C$————$C–COOH$ | | H H	H CH_3 |————| $CH_3–C$————$C–COOH$ | | H H	CH_3 | $CH_3–C$—— COOH | CH_3
Normal valeric acid, boils at 187°C.	β-methyl butyric or iso-valeric acid, boils at 177°C.	α-methyl butyric or methylethyl-acetic acid, boils at 174°C.	αα-dimethyl propionic or trimethylacetic acid, boils at 164°C.
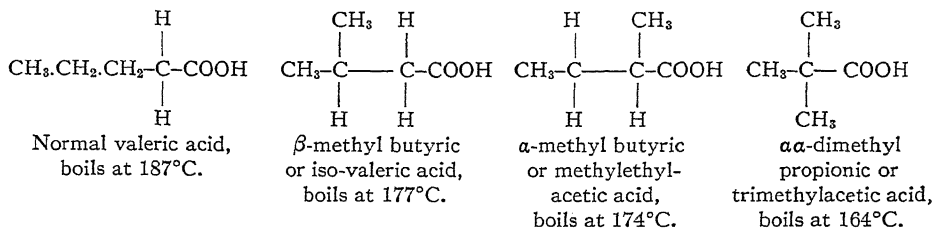
The three following compounds also have the same condensed formula $C_{16}H_{36}O_2$ but quite different physical and structural properties;

$C_{12}H_{25}O.CO.C_5H_{11}$ (lauryl caproate)
$C_6H_{13}O.CO.C_{11}H_{23}$ (hexyl laurate)
$C_{17}H_{35}.COOH$ (stearic acid).
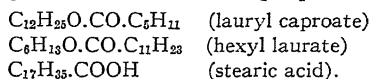
The glycerides joined by underlining in figure 1 present other examples of structural isomerism:

$CH_2.O.CO.C_{15}H_{31}$
|
$CH.OH$
|
CH_2OH
Glycerol α-palmitate, melts at 78°C.

CH_2OH
|
$CH.O.CO.C_{15}H_{31}$
|
CH_2OH
Glycerol β-palmitate, melts at 69°C.

Another example of structural isomerism is afforded by the difference in the positions of the two double bonds in the isomeric linolic acids represented by formulae (c) and (d) on page 16. Both have the same condensed formula $C_{18}H_{32}O_2$ but ordinary linolic acid (c) melts at a considerably lower temperature than its isomer (d).

The physical and chemical properties of structural isomers frequently are quite distinctly different, but isomeric glycerides differing only in the relative positions of the fatty acid radicals usually have very similar properties, a fact that renders the separation and recognition of individual fats in a mixture very difficult.

(b) GEOMETRICAL SPATIAL ISOMERISM

In compounds possessing the general structures

$$\frac{1}{2}>C=C<\frac{1}{2} \qquad \frac{1}{2}>C=C<\frac{3}{2} \qquad \frac{1}{2}>C=C<\frac{4}{3}$$
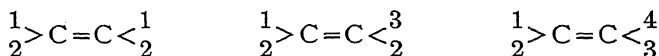
where 1, 2, 3, 4 represent different elements or groups, the double bond between the two carbon atoms tends to keep the positions of 1, 2, 3, 4 fixed in space. But any one of these compounds might have the atoms or groups oppositely attached to the right-hand carbon atom:

$$\frac{1}{2}>C=C<\frac{3}{2} \qquad \frac{1}{2}>C=C<\frac{2}{3}$$

Groups 2 on same side, or cis-form

Groups 2 on opposite side, or trans-form

21
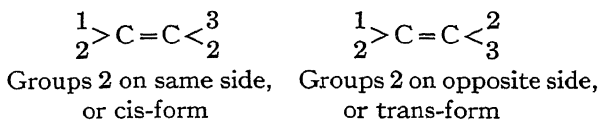
The above two compounds are *geometrically isomeric*, and are termed *cis-trans isomers*. Oleic acid, $CH_3(CH_2)_7CH=CH(CH_2)_7COOH$, can exist in the following two forms:

$$\begin{array}{cc} \underset{H}{\overset{CH_3(CH_2)_7}{>}}C=C\underset{H}{\overset{(CH_2)_7COOH}{<}} & \underset{H}{\overset{CH_3(CH_2)_7}{>}}C=C\underset{(CH_2)_7COOH}{\overset{H}{<}} \end{array}$$

Ordinary, or cis-oleic acid,   Trans-oleic acid (elaidic acid)
liquid at room temperature.   solid at room temperature.
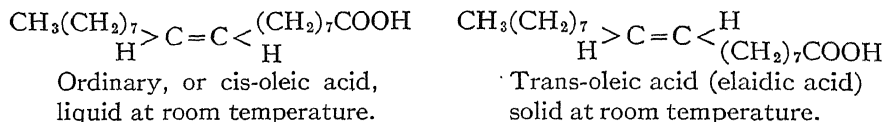
The transformation of oleic acid into elaidic acid takes place quite readily in the presence of certain reagents, the process being known as *elaidinization* (Section 5 I), even when applied to unsaturated fatty acids other than oleic.

(c) OPTICAL SPATIAL ISOMERISM

Carbon atoms attached by *single* bonds instead of by double bonds can also give rise to a type of spatial isomerism known as *optical isomerism* when all four atoms or groups attached to one of the carbon atoms are different:

$$2-\overset{\displaystyle 1}{\underset{\displaystyle 3}{C}}-4\ .$$
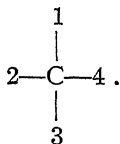
Details of this type of isomerism are not essential for the purposes of this Bulletin, and it need only be mentioned that the isomers are often practically indistinguishable except for a certain optical effect. Triglycerides of the type

$$(*)\ \begin{array}{l} CH_2O.CO.R_1 \\ | \\ CHO.CO.R \\ | \\ CH_2O.CO.R_2 \end{array}$$ commonly found in fats exhibit this effect to a weak degree
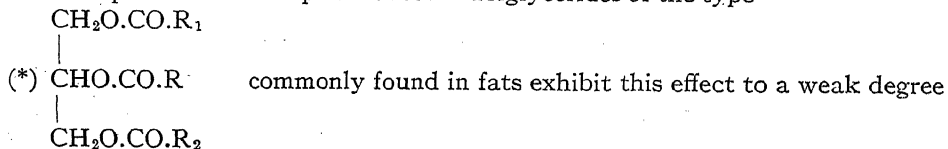
by virtue of the carbon atom designated by the (*) being linked by single bonds to the four different groups: H, $-O.CO.R$, $-CH_2O.CO.R_1$ and $-CH_2O.CO.R_2$.

IV. MISCELLANEOUS DEFINITIONS

Adsorption and absorption. If a solution of some material ("solute") in a solvent is brought into contact with a porous solid material such as charcoal or fuller's earth then the solution decreases in concentration, some of the solute being *adsorbed* or fixed to the surface of the porous solid material. In the case of *absorption* the solution, unchanged in concentration, penetrates through the porous solid, as when a salt solution is absorbed by a sponge. In the case of adsorption, the amount of solute taken up by the solid material depends upon the amount of surface exposed and the nature of that surface. When a solid is finely pulverized its surface is enormously increased; thus a glass plate that will adsorb a fine film of moisture from the air that cannot be removed by drying with

a cloth, will adsorb a great deal more moisture if finely pulverized. Clays, charcoals and many finely dispersed materials have strong adsorbent properties.

Catalysts are substances that hasten chemical reactions without themselves being used up during the reaction. They usually are effective in small concentrations and can be entirely recovered at the end of the reaction. Catalysts cannot initiate a reaction but once it has started, may increase the rate enormously. Examples of inorganic catalysts are nickel compounds that increase the rate of hydrogenation of oils, and cobalt salts that increase the rate of oxidation. Naturally occurring organic catalysts include substances known as *enzymes* that direct and control the reactions taking place in living organisms; they usually exist in the colloidal state.

During certain reactions substances may be formed that act as catalysts towards the initial reaction. Such a reaction is known as *autocatalytic* and if the amount of one of the products is plotted at various times the resulting graph shows a typical S-shaped curve. Usually there is a well-defined period where the reaction proceeds at a very slow rate followed by a period of very rapid reaction. The first period is known as the *inductive period* and is of particular importance in the study of the rancidification of oils.

Colloids. Substances in the *colloidal state* are in the form of ultra-microscopic particles of solids or liquids dispersed in another liquid, solid or gas, and the most important difference between colloidal solutions and "true" solutions is the fact that colloidal solutions must be looked upon as two-phase systems with a consequent interphase between the two phases. Since colloidal particles are very small the total interfacial surface of the dispersed material is very large and many of the peculiar properties of colloidal substances are due to this large surface, e.g. the phenomenon of adsorption. Theoretically any substance, if sufficiently subdivided and dispersed in an appropriate medium may be put into the colloidal state.

The most important types of colloids are the *sols, gels* and *emulsions. Sols* consist of a solid dispersed in a liquid; they can be subdivided into lyophilic (solvent loving) colloids such as water "solutions" of proteins, starches, agar, etc., and lyophobic (solvent hating) colloids such as gold or silver finely dispersed in water. If certain lyophilic sols are made concentrated enough they set to a jelly-like mass called *gels*. These may or may not possess elastic properties; examples of those gels with elastic properties are gelatine and soap gels, whilst those without elastic properties are exemplified by silicic acid and the hydroxides of metals such as aluminium, iron and tin. When the dispersed colloid and the dispersion medium are both liquid the system is called an *emulsion*, typical examples of which are water-in-oil mixtures and oil-in-water mixtures.

Condensation reactions as referred to in this Bulletin involve chiefly the combination of two or more large molecules with the elimination of water. A particular example is the condensation of glycerol with phthalic acid and fatty acids to form a resin of high molecular weight. Water is produced during the

reaction. Treatment of unsaturated oils in the presence of oxygen at high temperatures also results in condensation.

Exothermic reactions are those in which heat is produced during the reaction. The reaction between unsaturated oils and oxygen is exothermic as also is the hydrogenation of oils. *Endothermic* reactions are those that absorb heat. They are not commonly met with in the chemistry of fats and oils.

Peptization is the name given to the process in which an insoluble material is dispersed by means of a second substance called the peptizer. Usually the latter reacts chemically on the insoluble material causing it to form a colloidal solution. The action of alkalies on proteins is an example of peptization.

pH is a symbol used to represent the acidity or alkalinity of a solution. All acidities or alkalinities are referred to the concentration of hydrogen ions in the solution; the more hydrogen ions per unit volume, the more acid is the solution. Actually, pH is equal to the logarithm of the volume in litres of solution that contains 1 g. of hydrogen ions. In solutions that are exactly neutral it is found that 10,000,000 litres contain 1 g. of hydrogen ions and since the logarithm of 10,000,000 is 7 *the pH of neutral solutions is 7*. Alkaline solutions have a pH value above 7 and acid solutions have a pH below 7. A decrease or increase of 1 pH means an increase or decrease of 10 times the concentration of hydrogen ions.

Substitution and addition reactions. In a *substitution* reaction an element in one of the reacting molecules is replaced by an element or group of elements in the other and there are always two products of the reaction. As an example, when a hydrocarbon is treated with chlorine a hydrogen atom of the hydrocarbon is replaced by an atom of chlorine, the replaced hydrogen atom forming hydrogen chloride with the other atom of the chlorine molecule. In an *addition* reaction no substitution takes place and the two reacting molecules form a single product. This is exemplified when a molecule of chlorine reacts with the double bond of an unsaturated fatty acid. Each atom of the chlorine molecule attaches itself to one of the carbon atoms of the double bond thus forming a single addition product and without the production of hydrogen chloride.

Note on terminology for unsaturation. As a means of indicating the degree of unsaturation found in mixtures of fats or other fatty compounds, when a knowledge of the actual chemical composition of the mixture is lacking, a special terminology has come into general use in the chemical and technological literature dealing with fats. By hydrogenating or ascertaining the iodine value of a known amount of the mixture, an estimate of the *average* number of unsaturated double bonds per molecule of the substances is possible. Since each double bond represents a deficiency of *two* atoms of hydrogen as compared with a completely saturated molecule, the indicated presence of an average of one double bond per molecule is conventionally written as −2H. This does not imply that *every* molecule of the fatty substances has only one double bond; there may be present a mixture of *saturated* compounds with compounds having *more than one* double bond per molecule. Thus the statement that the constituent fatty acids of a fish oil possess an average unsaturation of −7H means that the majority of the acids probably have three or four double bonds, though the presence of acids having a greater or lesser unsaturation is not excluded.

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SECTION 2. STRUCTURE OF COMPONENT ACIDS AND COMPOSITION OF MARINE ANIMAL OILS

I. STRUCTURE AND PROPERTIES OF THE FATTY ACIDS

With but few exceptions the fatty acids that occur naturally in marine animal oils contain an even number of carbon atoms arranged in a straight chain with the acid (carboxyl) group at one end. These fatty acids are capable of forming salts (soaps) with metallic hydroxides or oxides, and esters with alcohols. The physical and chemical properties of these acids are dependent upon the composition and structure, that is, upon the number of carbon atoms in the molecule and the number and position of the double bonds. The lower acids up to C_{12} are volatile in steam but all of them can be distilled, with or without decomposition, at suitably low pressures. The acids up to and including C_{10} are soluble in water, the solubility decreasing with increasing carbon content. The C_{10} member is but slightly soluble and all higher members both saturated and unsaturated are practically insoluble in water. Some properties of fatty acids found in marine animal oils are given in tables I and II.

TABLE I. Saturated fatty acids found in marine animal oils

Acid	Formula	Neutralization equivalent	M.P. (°C.)	B.P. (°C.)
Iso-valeric...........	$C_5H_{10}O_2$	102.0	−51	174
Capric...............	$C_{10}H_{20}O_2$	172.1	31.5	269
Lauric...............	$C_{12}H_{24}O_2$	200.1	43.5	176/15 mm. 102/1 mm.
Myristic..............	$C_{14}H_{28}O_2$	228.2	53.8	250/100 mm. 122/1 mm.
Palmitic..............	$C_{16}H_{32}O_2$	256.3	62.5	215/15 mm. 139/1 mm.
Stearic...............	$C_{18}H_{36}O_2$	284.3	69.6	232/15 mm. 160/1 mm.
Arachidic.............	$C_{20}H_{40}O_2$	312.3	77	205/1 mm.
Behenic..............	$C_{22}H_{44}O_2$	340.3	82	306/60 mm.
Lignoceric...........	$C_{24}H_{48}O_2$	368.4	86	

(a) PHYSICAL PROPERTIES

Whilst all fatty acids must be classed as weak acids, it must be pointed out that the higher insoluble members, such as palmitic, stearic, etc., cannot be assumed to be weaker acids than the lower soluble members of the series. Referring to data obtained at Harvard University in 1930, Conant (1932) states: "The

results show that none of the higher acids is significantly weaker than the first few members of the series. The apparent weakness in aqueous solutions is, of course, the result of their insolubility."

TABLE II. Unsaturated fatty acids found in marine animal oils

Acid Common name	Geneva system	Formula	No. of double bonds	Position of double bonds	Iodine value	Neut. equiv.	Boiling point (°C.)
Caproleic	Decenoic.........	$C_{10}H_{18}O_2$	1	9	145.7	174.1	143-148/15 mm.
Lauroleic	Dodecenoic........	$C_{12}H_{18}O_2$	1	4 3	121.9	208.2	
Myristoleic...	Tetradecenoic......	$C_{14}H_{26}O_2$	1	9 5	112.2	226.2	
Palmitoleic	Hexadecenoic......	$C_{16}H_{30}O_2$	1	9	99.8	254.2	
Hiragonic	Hexadecatrienoic...	$C_{16}H_{26}O_2$	3	6, 10, 14	304.3	250.2	180-190/15 mm.
Oleic	Octadecenoic	$C_{18}H_{34}O_2$	1	9	89.9	282.2	285/100 mm. 153/0.1 mm.
"	"	"	1	11	89.9	282.2	
"	"	"	1	8	89.9	282.2	
Linolic	Octadecadienoic....	$C_{18}H_{32}O_2$	2	9, 12(?)	181.1	280.2	228/14 mm.
Linolenic	Octadecatrienoic ...	$C_{18}H_{30}O_2$	3	9, 12, 15(?)	273.7	278.2	232/17 mm.
Moroctic	Octadecatetraenoic .	$C_{18}H_{28}O_2$	4	4, 8, 12, 15	367.5	276.2	
Gadoleic	Eicosenoic.........	$C_{20}H_{38}O_2$	1	9	81.7	310.3	220/6 mm.
....	Eicosatetraenoic....	$C_{20}H_{32}O_2$	4	4, 8, 12, 16	333.7	304.2	
....	Eicosapentaenoic...	$C_{20}H_{30}O_2$	5	4,8, 12, 15, 18	419.9	302.2	
Cetoleic	Docosenoic........	$C_{22}H_{40}O_2$	1	11	75.0	338.3	
Clupanodonic	Docosapentaenoic ..	$C_{22}H_{34}O_2$	5	4, 8, 12, 15, 19	384.2	330.3	236/5 mm.
....	Docosahexaenoic....	$C_{22}H_{32}O_2$	6	....	463.8	328.3	
Selacholeic	Tetracosenoic......	$C_{24}H_{46}O_2$	1	15	69.2	366.4	
....	Tetracosatetraenoic	$C_{24}H_{40}O_2$	4	....	281.7	360.3	
Socliodonic	Tetracosapentaenoic	$C_{24}H_{38}O_2$	5	....	354.2	358.2	
Nisinic	Tetracosahexaenoic.	$C_{24}H_{36}O_2$	6	....	427.5	356.2	

Although the higher members of the fatty acid series are insoluble in water they exhibit an interesting property when dispersed in this medium, namely that of orientation. If a solution of a fatty acid in some volatile solvent is placed on water and the solvent allowed to evaporate, the fatty acid molecules in the thin film left on the surface of the water tend to orientate themselves so that the acid or carboxyl groups are in the water and the carbon chains on the surface. This is due to the water having a greater attraction for the carboxyl group than for the carbon chain. This phenomenon of orientation makes itself evident in various ways when working with fatty acids. For instance, in some cases, if an aqueous solution of sodium or potassium soaps of mixed fatty acids is acidified with an inorganic acid, the liberated fatty acids may remain opaque and finely dispersed at temperatures much above their melting point for considerable lengths of time. This is due to the orientation of the free fatty acids around small masses of water which remain dispersed in the acidified water and thus make clarification and separation of the free fatty acids difficult. Orientation of fatty acids also appears to be responsible for another phenomenon recently investigated in these laboratories and concerns the loss of vitamin A when an oil containing this vitamin is heated and intimately mixed with water. As long as there are no free fatty acids present in the oil there is no loss of vitamin A. However, in the presence of free

fatty acids the oil loses some vitamin A, presumably through adsorption on the free fatty acids surrounding the masses dispersed in the water. This will be referred to in more detail in a later section.

The melting points of the saturated fatty acids of even carbon number above C_6 increase regularly with increasing number of carbon atoms. Until recently there was some doubt as to whether the C_{20} and C_{24} members (arachidic and lignoceric acids) might not have branched chains since their melting points did not show normal values. X-ray analysis now shows that they are normal straight chain acids and that previous work on melting points was probably done on impure samples. It should be noted that the solid saturated fatty acids crystallize in two forms; the alpha or unstable form appears when the acid first solidifies and this then changes over into the beta or stable form when the temperature is lowered slightly below the solidification point. The beta form has the lower melting point and will not change over into the alpha form again without first melting. This phenomenon is of importance in determining the melting point of a solid or mixture of solid fatty acids. After the sample has solidified it should be given sufficient time at a temperature below its solidification point for complete transformation into the beta form. The melting point of the latter is then determined.

Unsaturation has a profound effect on the melting point of fatty acids. In the C_{18} series the saturated member, stearic acid, melts at 71°C., whilst oleic, linoleic and linolenic acids with one, two and three double bonds melt at 16, -14 and -30°C. respectively. In addition to the number of double bonds the position of such bonds in the carbon chain also affects the melting point. For example, in the C_{18} series, ordinary oleic acid has its double bond between the ninth and tenth carbon atoms, that is, in the middle of the chain. As the double bond is shifted in either direction the melting point increases. The known isomers of oleic acid have double bond positions and melting points as follows:

Position of double bond—2:3, 3:4, 4:5, 6:7, 9:10, 10:11.
Melting point (°C.)—   59, 56, 52, 33, 16,   44.

Geometrical isomerism also affects the melting point (Section 1, page 21). The trans-form usually has the higher melting point. Theoretically this geometrical isomerism can occur at each double bond. The possible complexity of the unsaturated fatty acids with more than one double bond will thus be realized.

The boiling points of the fatty acids increase with increasing carbon content. Beginning with the C_{10} member distillation without excessive decomposition can be accomplished only under reduced pressures. Unsaturation has not the same effect on the boiling point as it has on the melting point. Investigation has shown that fatty acids of the same carbon content boil at practically the same temperature irrespective of the degree of unsaturation (Guha, Hilditch and Lovern 1930).

Saturated fatty acids, and most probably unsaturated fatty acids, crystallize in pairs with the two carboxyl groups adjacent. They maintain this association to a degree in solution depending upon the nature of the solvent. This point

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is of importance when determining molecular weights by the freezing or boiling point methods. Unsaturation tends to decrease this association (Brocklesby 1936).

(b) CHEMICAL PROPERTIES

The chemical reactions of the fatty acids can be divided into two classes: those that are typical of the acid or carboxyl group, and those typical of the carbon chain. By means of the acidic replaceable hydrogen in the carboxyl group these acids can form salts (soaps) with basic oxides, hydroxides and carbonates. With alcohols they form esters; natural fats and oils are esters of the trihydric alcohol, glycerol. These two classes of compounds of the fatty acids, salts and esters, are by far the most important commercial derivatives of the fats and oils. A less important reaction of the carboxyl group, utilized in the technical treatment of fatty acids or neutral fats and oils, consists in the reduction of the carboxyl group to the alcohol group by treatment with hydrogen at high temperatures and pressures in the presence of catalysts; lauryl alcohol is obtained from lauric acid, palmityl alcohol from palmitic acid and so on. These higher alcohols are used as detergents. Another class of detergent is obtained by the action of hydroxyethanesulphonic acid (isethionic acid) on fatty acids giving sulphonated esters which can be used in acid media. Other reactions of the carboxyl group of fatty acids are of little industrial interest.

The chemical reactions that take place in the carbon chain are practically restricted to the double bonds in unsaturated acids. The saturated carbon chain is very stable, being attacked very slowly by oxidizing reagents. The halogens, particularly bromine and chlorine, give rise to substitution products.

The most important reactions of the double bonds in unsaturated fatty acids are briefly as follows:

Oxidizing reagents. Unsaturated acids absorb oxygen to form oxides or peroxides. Under suitable conditions these may break down giving an acid and an aldehyde. The more unsaturated the fatty acid the more easily is it attacked by oxygen or other oxidizing reagents. Ozone forms ozonides, which, on boiling with water, also split up to give acids and aldehydes. It is to be noticed that oxidizing reagents split the carbon chain at the double bond. By identification of the scission products it is therefore possible to ascertain the position of such bonds in the chain. The most useful oxidizing reagent is potassium permanganate, preferably in acetone solution.

Halogenating reagents. Bromine and iodine add at the double bond gi ing substituted fatty acids. In suitable solvents bromine forms bromo-compounds that can be used for identification purposes. Mixed halogen reagents, such as iodo-chloride, are used to determine the extent of unsaturation of oils, the results being expressed in per cent of iodine absorbed, i.e. the so-called "iodine value".

Halogen acids, particularly hydrogen iodide and hydrogen bromide, add directly at the double bond. They are not used for analytical purposes.

Hydrogenation. With suitable catalysts hydrogen adds at the double bond giving saturated products. This reaction forms the basis of an important process wherein liquid oils are converted into solid fats.

Sulphuric acid reacts at the double bond in unsaturated fatty acids to give a variety of products dependent upon reaction conditions. The product of greatest industrial value is that in which the sulphuric acid itself is attached directly at the double bond giving sulphuric esters.

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Nitrous oxide when bubbled through unsaturated acids forms unstable addition compound which immediately break up to give a mixture of the trans- and cis-form isomers. The trans-acid is formed to the extent of about 66 per cent.

Other reactions of the double bond in fatty acids that are more concerned with the technical processing of fats and oils will be discussed in Section 5.

(c) SALTS OF THE FATTY ACIDS

The ammonium, potassium and sodium salts of the fatty acids comprise the detergent soaps of commerce. The solubility of these soaps in water decreases in the order named. Solubility decreases with increase in molecular weight of the fatty acid, and increases with rise in temperature of the solution, and with the number and complexity of the double bonds in the fatty acid. The geometrical structure of the acid has also an effect on solubility, the trans-form usually being less soluble than the cis-form, i.e. sodium elaidate is less soluble than sodium oleate. The sodium soaps of the saturated acids above palmitic in the series are almost insoluble in cold water.

The chief characteristic of the alkali metal salts of the higher fatty acids, however, is their detergent properties. The sodium salts of the fatty acids lower in the series than lauric show little if any soap-like properties. With lauric acid they are well developed. If the salt of a fatty acid goes into true solution, such a solution is not a detergent. If, however, the salt gives a colloidal solution, then detergent properties will be shown. Among the colloidal properties exhibited by soap solutions is that of absorbing water to form a gel. Gelling properties start with sodium laurate and increase very rapidly with increasing molecular weight of the fatty acid, that is, the higher the molecular weight of the fatty acid the more water will its sodium salt absorb to form a stiff gel. Unsaturation decreases this "gelation capacity", the sodium soaps of stearic, oleic and linoleic acids absorbing 88.0, 3.2 and 3.3 cc. of water per gram of dry soap. The soaps of the trans-form of the geometrical isomers have higher gelation capacities than the cis-forms, viz. sodium elaidate and sodium oleate absorb 30.0 and 3.2 cc. of water per gram of soap.

The water-soluble soaps stabilize oil-in-water types of emulsions. On the other hand the soaps of the alkaline earth metals, calcium, strontium and barium and also magnesium, tend to be more soluble in oil than they are in water and stabilize the water-in-oil type of emulsion. The solubilities of the alkaline earth soaps in oil are, in general, affected by the same conditions as affect the alkali soaps in water. Increasing unsaturation of the fatty acid increases the solubility of the soap in oil as also does increase in temperature of the solution.

Copper, iron, cobalt, manganese, lead, cerium, zinc and aluminium salts of the fatty acids are also soluble to some extent in oils but are practically insoluble in water. Here again, the more unsaturated the fatty acid the more soluble will be the metallic soap in oil. The various applications of these soaps are considered in more detail in Section 9, page 359.

Of particular interest, from the analytical standpoint, are the solubilities of the lead, lithium and sodium soaps of the fatty acids in non-aqueous solvents, as

they permit a fairly sharp separation of various types of acids. In 95 per cent alcohol the lead soaps of the saturated fatty acids are soluble up to the myristate (C$_{14}$) which is distinctly soluble, whereas the palmitate is practically insoluble. All the lead soaps of the unsaturated acids up to C$_{18}$ are freely soluble in 95 per cent alcohol; those of the fatty acids of higher molecular weight with one or two double bonds are but sparingly soluble; with three or more double bonds the lead salts of the fatty acids of high molecular weight are soluble.

The lithium and sodium salts of unsaturated fatty acids with three or more double bonds are freely soluble in 95 per cent acetone, those with one or two double bonds are sparingly soluble and those of the saturated acids are insoluble. Although the differences in solubility are not clear-cut, they afford a means of isolating highly unsaturated fatty acids from a complex mixture.

(d) The Saturated Fatty Acids

Iso-valeric acid. Characteristic odour. Soluble in 23.6 parts of water at 20°C. Sodium salts very soluble and not salted out by sodium chloride. Found in head oil of porpoises and dolphins.

Capric acid. Very slightly soluble in water. Volatile in steam. Lead salts soluble to 0.03% in ether at 20°C. Head oil of sperm whale contains about 3.5%.

Lauric acid. Insoluble in water but easily soluble in ether and alcohol. Will distill at ordinary pressures without decomposition. Volatile with steam. Lead salt melts at 104.6°C., and is practically insoluble in ether, but in alcohol 0.05 parts at 15° and 2.35 parts at the boiling point are dissolved in 100 parts of the solvent. Alkali salts possess detergent properties. Head oil of sperm whale contains 16%.

Myristic acid. Insoluble in water. Easily soluble in ether, alcohol and chloroform. Lead salt practically insoluble in cold ether. Sperm whale head oil contains about 14%. The acid is present in smaller amounts in many other marine animal oils.

Palmitic acid. One hundred parts of absolute alcohol dissolve 9.32 parts of the acid at 19.5°C. Lead salt insoluble in cold ether and cold alcohol. Chief saturated fatty acid in marine animal oils.

Stearic acid. Soluble in 40 parts of cold alcohol and in one part of boiling alcohol. Lead salts insoluble in cold alcohol and ether. Found in marine animal oils from traces to about 3%.

Arachidic acid. Soluble in hot absolute alcohol. Small amounts are claimed to have been isolated from Japanese herring oil. Produced by hydrogenating some fish oils.

Behenic acid. Very slightly soluble in cold alcohol and ether. Found in traces in sardine and herring oils and produced by hydrogenating some fish oils.

(e) The Unsaturated Fatty Acids

Caproleic or decenoic acid. Melts below 0°C. Isolated from sperm whale head oil.

Lauroleic or dodecenoic acid. Liquid at room temperature. Isolated from sperm whale head oil.

Myristoleic or tetradecenoic acid. Lead salt soluble in cold 95% alcohol. 9:10 variety found in South Georgia whale oil. 5:6 variety in head oil of sperm whale.

Palmitoleic, physetoleic, or hexadecenoic acid. Melts at −1°C. Lead salt freely soluble in cold 95% alcohol. Found in most marine animal oils in amounts varying from 10 to 25%.

Hiragonic or hexadecatrienoic acid. Forms a hexabromide which is soluble in benzol at 40°C. Has been isolated from Japanese sardine oil.

Oleic or octadecenoic acid. Crystallizes in two forms m.p.'s 12 and 17°C. Insoluble in water but easily soluble in most organic solvents. Forms an oily dibromide. Naturally occurring acid

is the cis-form. 9:10 variety occurs in nearly all marine animal oils. 11:12 variety probably present to small extent in whale oils. 8:9 and 11:12 varieties occur in hydrogenated fish oils.

Linoleic or octadecadienoic acid. This acid has two double bonds and yields stearic acid on hydrogenation. The linoleic acid commonly occurring in vegetable oils has the two double bonds in the 9:10 and 12:13 positions. There are four possible geometrical isomeric forms. The acid forms two tetrabromides, one insoluble and one soluble in petroleum spirits. Linoleic acid is one of the so-called "essential fatty acids." (See Section 4, page 103.) The occurrence of this acid in marine animal oils is a matter of some doubt.

Linolenic or octadecatrienoic acid. Has three double bonds in the 9:10, 12:13 and 15:16 positions. This acid is the most important acid in drying oils. It forms two hexabromides, one soluble and one insoluble in ethyl ether. Hydrogenates to stearic acid. Can function as an essential fatty acid. Linolenic acid has recently been isolated from cod liver, shark liver and whale oils. Probably occurs in small amounts in most marine animal oils.

Moroctic or octadecatetraenoic acid. Has four double bonds in the 4:5, 8:9, 12:13 and 15:16 positions. Has been isolated from Japanese sardine oil.

Gadoleic or eicosenoic acid contains one double bond probably in the 9:10 position. Yields arachidic acid on hydrogenation. Has been isolated from cod liver, herring, sardine and whale oils and is probably present in most marine animal oils. The lead salt of this acid is but sparingly soluble in 95% alcohol.

Eicosatetrenoic acid with four double bonds has been isolated from sardine oil. The double bonds are probably in the 4:5, 8:9, 12:13, and 16:17 positions.

Eicosapentaenoic acid with five double bonds has been isolated from Japanese sardine oil. Double bonds are given as being in following positions: 4:5, 8:9, 12:13, 15:16 and 18:19.

Cetoleic or docosenoic acid has one double bond in the 11:12 position and is usually associated with gadoleic acid in marine animal oils. Lead salt but sparingly soluble in 95% alcohol.

Clupanodonic or docosapentaenoic acid has five double bonds probably in the following positions: 4:5, 8:9, 12:13, 15:16, 19:20. Forms a solid decabromide and iodochloride, insoluble in most organic solvents. Hydrogenates to behenic acid. Usually isolated by means of its bromide or iodochloride or by its sodium or lithium salts in acetone. The iron, magnesium, aluminium, manganese, cobalt, nickel, zinc, copper and lead salts are, in the main, soluble in ether, petroleum spirits and benzene. Clupanodonic acid occurs in practically all marine animal oils.

Docosahexaenoic acid contains six double bonds. Properties and structure not known. Former probably similar to clupanodonic acid. Has been isolated from Japanese sardine oil.

Selacholeic or tetracosenoic acid contains one double bond in the 9:10 position. Found chiefly in liver oils of sharks.

Socliodonic or tetracosapentaenoic acid with five double bonds has been isolated from Japanese sardine oil.

Nisinic or tetracosahexaenoic acid with six double bonds has recently been isolated from Japanese sardine oil. Preliminary work shows double bonds to be adjacent to the 4th, 8th, 12th, 15th, 18th and 21st carbon atoms. Sodium salt soluble in 95% acetone.

II. OCCURRENCE AND COMPOSITION OF MARINE ANIMAL OILS

(a) OCCURRENCE

Marine animal oils of commercial importance are obtained chiefly from two large biological groups,—*cetaceans* (a group of marine mammals which includes whales, porpoises and dolphins) and *fishes*. The group of marine mammals known as pinnipedes and including seals, sea lions, etc., will not be included in this discussion. In cetaceans most of the body fat is contained in the blubber or fatty

layer under the skin. In addition to blubber fat the sperm whale (Physeteridae) also contains considerable amounts of oil in certain cavities of the head. Both the blubber and head oil of the sperm whale differ in composition from the blubber of the right whales (*Balaena*) or of the rorquals (*Balaenoptera* and *Megaptera*). In porpoises and dolphins (Delphinidae) the jaw and head contain an oil which differs from that found in the blubber. Cetacean livers, like mammalian livers in general, contain only a small amount of fat.

The cetaceans are warm-blooded animals and the large amounts of blubber found in them would suggest that its primary function is one of insulation against heat losses. Cold-blooded animals do not possess a heavy subcutaneous layer of fatty material.

In the fishes, we are concerned with the oil of two classes. The Teleostomi or true fishes have a calcified internal skeleton. This group includes such well-known fishes as the salmon, herring, cod, halibut, etc. The Elasmobranchii, which includes the sharks and rays, have a cartilaginous internal skeleton. The ratfishes (Holocephali) are closely related to this group.

In most fishes fat is found in a thin adipose tissue beneath the skin, throughout the muscle and connective tissue, in the liver, eggs, mesentery, and intestine. However, the amount and nature of the fat in these depots vary greatly.

In the Teleostomi or true fishes the chief fat depot may be either in the muscle tissue, in the liver or in parts of the intestine. Some fishes, such as the cod, haddock, ling and others, possess fairly large oily livers which contain almost all of the fat of the fish, the muscle tissue being very low in fat. On the other hand many fishes, notably the salmon, sardine, pilchard, etc., possess relatively small livers with little oil in them, but have a very oily muscle tissue. In general, bony fishes with an oily liver have a relatively small amount of fat in the muscle tissue. Conversely, fishes with a large amount of oil in the muscle tissue contain little in the liver. As an example, the halibut contains from 8 to 25 per cent oil in the liver but less than 1 per cent in the muscle tissue. (It may be noted in passing that the halibut contains considerable oil in the muscle tissue of the head and in a thin layer just below the skin.) Salmon, however, may have as high as 20 per cent oil in the muscle tissue, but the liver seldom contains more than 5 per cent of fat. Obviously, since the fat content of all depots varies with the season and/or sexual maturity, the above generality does not always apply.

Little is known about the fat content of other tissues. Halibut, ling cod and black cod have variable amounts of fat in the intestine and mesentery, and certain fishes have a subcutaneous fatty tissue between the skin and muscle tissue. Large amounts of oil are found in the eggs of salmon. This oil differs considerably in properties and composition from that in the other fat depots of this fish.

The Elasmobranchii, in the main, possess large and very oily livers. In some, such as the dogfish (*Squalus sucklii*), the livers may constitute from 10 to 15 per cent of the weight of the fish and the oil content rarely recedes below 60 per cent.

The muscle tissue, on the other hand, also contains considerable amounts of oil. Most of the larger sharks have very large and oily livers and many have been fished commercially for their liver oil. The livers of the Rajidae (skates and rays) and of the Chimaeridae (ratfishes) are also very oily.

(*b*) COMPOSITION

Our knowledge of the composition of marine animal oils has been extended considerably during the past few years through the consistent application of the methyl-ester fractionation method of analysis. Although a great many fragmentary analyses have been reported in the literature, most of the complete analyses done by the above method are due to Professor T. P. Hilditch and his co-workers at Liverpool, and to Dr. J. A. Lovern, Torry Research Station, Aberdeen. Most of the data given in this section are from reports written by these two investigators. Recent work by Farmer and Van den Heuvel (1938) suggests that some reduction in unsaturation takes place during high vacuum distillation of the highly unsaturated esters. It is possible, therefore, that the average unsaturation for the C_{20}, C_{22} and C_{24} components, given in the following data, is slightly lower than that actually obtaining in the original oils.

In fish oils, fatty acids with from 14 to 24 carbon atoms are found; the unsaturation is not usually greater than $-2H$ in the C_{14} and C_{16} series, $-4H$ in the C_{18} series (Section 1, page 24 has the explanation of this terminology), but in the C_{20}, C_{22} and C_{24} series may exceed $-10H$. The latter highly unsaturated fatty acids are more or less characteristic of aquatic organisms. The total saturated fatty acids may vary from 10 to nearly 30 per cent, of which palmitic acid forms the greater part. The unsaponifiable matter may vary both in composition and quantity through wide limits (Section 3). In some species the unsaponifiable matter is always less than 1 per cent whilst in others it may reach 80 per cent.

In table III will be found analyses of oils from some Teleostomi or true fishes. In these oils the unsaponifiable matter rarely exceeds 1 per cent. The saturated fatty acids vary from 11 to 26 per cent (based on the total fatty acids present). A comparison of the total saturated fatty acids in the liver oils with those in the body oils is of interest. The mean per cent of the former (13 samples) is 18.3 and of the latter (8 samples) 22.2 per cent. The difference between these means (3.9 per cent) appears to be statistically significant. As far as these data are concerned, therefore, we can assume that the body fat of the Teleostomi contains a greater quantity of saturated fatty acids than the liver fat. In both body and liver oils, palmitic acid (C_{16}) is the chief saturated component varying in both types of oil from about 8 to 18 per cent. Myristic acid (C_{14}) occurs in the liver oils in amounts varying from 2 to 7 per cent, except in tuna liver oil where it is absent entirely. In the body oils the range of myristic acid is from 4 to 7 per cent. It is present in the body oil of the tuna. Stearic acid (C_{18}) occurs only in minor amounts in both types of oil, again with the exception of tuna liver oil where it is present in the amount of 8.9 per cent.

Considering now the unsaturated fatty acids of Teleostomi body and liver

oils it will be observed that in the C_{14} series the highest unsaturation is $-2H$, that is, the unsaturated C_{14} component is exclusively myristoleic acid. In the C_{16} series the unsaturation exceeds $-2H$ in some oils and thus, whilst palmitoleic acid is the chief component, small amounts of more highly unsaturated C_{16} acids may occur, i.e. hiragonic acid with three double bonds ($-6H$) has been isolated from

TABLE III.*   Weight percentage composition of fatty acids in fish oils

Sub-class Teleostomi

	Unsap. matter %	Saturated			Unsaturated				
		C_{14}	C_{16}	C_{18}	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}
Family Acipenseridae Atlantic sturgeon, *Acipenser sturio*,									
peritoneal	–	7.1	14.0	0.8	0.6	23.8	35.8(2.9)	12.1(7.4)	5.8 (8.6)
pancreas	–	4.5	16.4	1.1	nil	21.4	36.7(2.9)	14.5(6.8)	5.4 (9.1)
liver	–	3.0	19.2	nil	nil	19.5	39.6(2.7)	11.8(7.1)	6.9(10.0)
Family Clupeidae (body oil) Pacific pilchard, *Sardinops caerula* (b)	1.0	5.1	14.4	3.2	Trace	11.7(2)	17.6(3.3)	17.9(4.1)	13.8 (8.5) C_{24} 15.2(10.9)
Jap. sardine, *Sardina melanostica* (a)	–	5.8	9.7	2.3	–	13.0(2)	24.2(?)	26.0(5) C_{24}	19.0(5)
Menhaden, *Brevoortia tyrannus* (a)	–	5.9	16.3	0.6 (C_{20} & C_{22} 1.4)	–	15.5(2)	29.6(4)	19.0(10)	11.7(10)
Sprat (Europe), *Clupea sprattus*	0.9	6.0	18.7	0.9	0.1	16.2	29.0(2.9)	18.2(5.6)	10.9(7.1)
Family Salmonidae Atlantic salmon, *Salmo salar* (liver)	–	2.7	10.9	1.6	0.7	12.3(2)	32.8(2.9)	25.5(5.7)	13.2(7.8)
Sea trout (Europe) *Salmo trutta* (body)	–	2.2	17.0	4.0	0.1	8.8(2.4)	26.3(3.0)	19.7(6.6)	19.0(9.2) C_{24} 2.5(?)
Family Scombridae Bluefin tuna (tunny), *Thunnus thynnus*,									
flesh	–	4.2	18.6	3.5	–	6.2(2.7)	26.0(3.2)	23.5(5.5)	18.0(6.8)
liver	–	–	17.9	8.9	–	3.4(2.5)	23.5(2.8)	28.2(5.5)	18.1(7.4)
Family Merluccidae Hake (Europe) *Merluccius* sp. (c)									
liver	0.9	7.0	13.0	–	Trace	17.0(2)	18.0(3.5)	31.0(4.9)	14.0(?)
Family Gadidae Pollack, *Pollachius virens*,									
liver		2.1	13.0	1.4	–	10.9	34.2(2.7)	25.4(5.4)	13.0(6.5)
Cod (Atlantic), *Gadus callarias* (c)									
Newfoundland, liver	0.9	6.0	8.5	0.5	Trace	20.0(2.3)	29.0(2.8)	26.0(6.0)	10.0(6.9)
Scottish, "	1.0	3.5	10.0	–	0.5	15.5(2)	25.0(2.9)	31.5(6.1)	14.0(6.4)
Norwegian, "	0.6	5.0	6.5	Trace	0.5	16.0(2)	31.0(2.8)	30.5(5.1)	10.5(?)
Coal-fish (Europe), *Gadus virens* (c) liver	0.8	6.5	13.0	0.5	Nil	14.5	31.0	24.5	10.0
Haddock (Atlantic), *Melanogrammus aeglifinus*, liver	0.7	4.3	14.1	0.3	0.5	12.4	30.5(2.6)	29.3(5.9)	8.6(7.3)
Ling (Atlantic), *Molva molva* (c), liver	1.1	5.0	13.0	1.0	Trace	13.0(2)	32.5(2.8)	24.0(5.7)	11.5(7.0)
Family Pleuronectidae Halibut, *Hippoglossus* sp.									
liver (c)	– 6.6	3.9	15.1	0.5	Nil	18.7	34.4(2.0)	13.8(5.5)	13.6(7.6)
body (c)	–	4.0	14.8	0.7	Trace	6.5(2.6)	23.8(3.0)	26.9(5.2)	23.3(6.5)
Turbot, *Scophthalmus maximus*, liver (c)	–	7.6	14.9	0.8	1.5	21.4(2.1)	27.1(2.5)	14.0(6.1)	12.7(6.7)
Family Lophiidae Angler (Atlantic), *Lophius piscatorius* (c), liver	1.0	4.9	9.6	1.3	0.4	12.1	30.9(3.3)	24.9(5.9)	15.9(8.6)

*The data in tables III, IV and V are largely from Lovern's work. The exceptions are: (*a*) Armstrong and Allan (1924); (*b*) Brocklesby and Harding (1938); (*c*) Guha, Hilditch and Lovern (1930); (*d*) Hilditch and Houlbrooke (1928); (*e*) Williams and Maslov (1936).

Japanese sardine oil. In the C_{18} series the chief component is oleic acid with one double bond ($-2H$) but in this series the average unsaturation is much higher than in the C_{16} series. The C_{18} acids more unsaturated than oleic that have actually been isolated from fish oils include linolenic acid with three double bonds ($-6H$) and moroctic acid with four double bonds ($-8H$). Linolic acid with two double bonds has recently been shown to be absent in a number of fish oils. In the higher series the average unsaturation varies from $-4H$ for C_{20} to $-10.9H$ for C_{24}. The higher the carbon content of the fatty acid the higher is the potential

unsaturation. There is but little difference between the unsaturated acid composition of the body and liver oils. The total amount of C_{20} and C_{22} acids in both is almost the same and the average unsaturation is not significantly different. However, the difference in behaviour between body and liver oils during technical processing, as for instance the polymerization by heat or the nature of the film on "drying", shows that the highly unsaturated acids in these two types of oil must be different and this difference probably lies in the actual structure of the acids themselves. Guha, Hilditch and Lovern (1930) observed a difference in susceptibility to heat polymerization of the esters of highly unsaturated acids from various liver oils of identical or closely related species.

TABLE IV. Weight percentage composition of fatty acids in fish liver oils

Sub-Class Elasmobranchii

	Unsap. matter %	Saturated			Unsaturated					
		C_{14}	C_{16}	C_{18}	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}	C_{24}
Family Squalidae										
Dogfish (Atlantic), Squalus acanthias (c)	10.5	6	10.5	3	–	9(2.0)	24.5(2.3)	29.0(3.3)	12.0(4.0)	6(2)
Dogfish (Atlantic), Centrophorus sp. (d)	50-80	1.0	13.0	2.5	trace	3.5(2.0)	35.5(2.1)	16.5(2.2)	16.0(2.3)	12(3)
Family Scymnorhinidae										
Shark (Europe), Scymnorhinus lichia (d)	70-80	1.0	14.5	3.5 (C20 1%)	0.5	4.0(2.0)	29.0(2.0)	10.5(2.0)	26.0(2.1)	10(2)
Family Scylliorhinidae										
Spotted dogfish, Scyllium canicula	2.2	1.7	15.7	3.3	–	4.0(2.2)	25.3(3.0)	24.4(6.4)	24.8(9.2)	Trace?
Family Alopiidae										
Thresher shark, Alopecia vulpes	1.8	7.5	11.0	0.5	1.5	12.0(2.0)	19.0(3.4)	31.0(6.6)	17.5(10.5)	–
Family Squatinidae										
Monk-fish, Squatina angelus	1.4	1.4	17.0	2.0	–	6.5(2.0)	20.7(3.0)	21.9(6.0)	30.5(10.2)	–
Family Rajidae										
Skate, Raja maculata (c)	0.3	4.0	14.0	–	trace	10.5(2.0)	20.5(3.3)	32.5(7.3)	18.5(9.5)	–
Sub-Class Holocephali										
Family Chimaeridae										
Ratfish, Chimaera monstrosa	37.5	–	8.4	7.2*	–	2.5	50.6(2.2)	19.6(2.9)	7.9(3.5)	2.1(?)

*Plus 1.3% C_{20} and 0.4% C_{22}.

In table IV will be found representative analyses of the liver oils of the Elasmobranchii (sharks and rays) and of the Holocephali (ratfishes). Tsujimoto (1932) has divided elasmobranch liver oils into at least three groups as follows: (1) those in which the unsaponifiable matter does not exceed 1 to 2 per cent, and which consists mainly of sterols, (2) those containing from 10 to 30 per cent unsaponifiable matter consisting mainly of chimyl, batyl and selachyl alcohols and (3) those with very large amounts of unsaponifiable matter (50 to 80 per cent) containing large amounts of the unsaturated hydrocarbon squalene. On the basis of this division it is found that the fatty acid compositions show some well defined differences. The four samples with unsaponifiable matter up to about 2 per cent (spotted dogfish, thresher shark, monkfish and skate) have unsaturated fatty acids similar to those of the liver oils of the Teleostomi. In particular the C_{20} and C_{22} acids are highly unsaturated. On the other hand the two samples with high content of unsaponifiable matter [dogfish (*Centrophorus*) and

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shark] have C_{20} and C_{22} acids which are mainly monoethylenic, and in addition contain monoethylenic C_{24} acids. The dogfish, *Squalus*, with about 10 per cent unsaponifiable matter content, contains unsaturated acids which are approximately intermediate between the two extremes, both in regard to the unsaturation of the C_{20} and C_{22} acids and also in the amount of C_{24} acids. Ratfish liver oil, containing 37.5 per cent of unsaponifiable matter (containing no squalene), belongs definitely to the third group in Tsujimoto's classification and the higher unsaturated acids are largely monoethylenic.

The total amount of saturated fatty acids is not significantly different in those liver oils of low and high content of unsaponifiable matter. There is, however, less myristic and more stearic acid in those oils with large amounts of unsaponifiable matter. In addition, two oils in the latter group also contain small amounts of the saturated C_{20} acid and one of them also contains a slight amount of saturated C_{22}.

It was originally suggested by Guha, Hilditch and Lovern that there was a relationship between the fatty acid composition of oils from the elasmobranchs and the presence or absence of the hydrocarbon squalene. Tsujimoto (1932) and also Lovern (1937) showed that this is not so, and that oils with low unsaturated C_{20} and C_{22} acids do not necessarily contain squalene in the unsaponifiable matter, e.g. ratfish liver oil.

The last group of oils to be considered here is that of the cetaceans, some analyses of which are given in table V. The blubber oils of the Balaenidae or "right" whales resemble the liver oils of the Teleostomi (particularly those of the Gadidae) in composition. The most notable difference is in the unsaturated C_{18} group. In whale oils these components represent approximately 30 to 45 per cent of the total fatty acids, an amount higher than found in the liver oils. As a consequence the amount of unsaturated C_{20} and C_{22} acids is less in the whale oils than in the liver oils but the degree of unsaturation remains approximately the same.

The head and blubber oils of the sperm whales are noted for the large amount of higher alcohols that they contain (Section 3). In addition, however, the fatty acid compositions are markedly different from those of other marine animal oils. In the head oil are found considerable quantities of capric, lauric and lauroleic acids. The unsaturated acids are exclusively monoethylenic, in which the C_{14}, C_{16} and C_{18} acids predominate. Unsaturated C_{20} acids are present only in small amounts and the C_{22} series is absent altogether. In the blubber oil stearic acid is absent but a small quantity of lauric acid occurs. In the unsaturated acids an unusually large amount of palmitoleic acid is present (approximately 25 per cent) together with the usual amount of oleic acid. The C_{20} acids in the blubber oil are slightly more unsaturated than those of the head oil and in addition there occurs a small amount of C_{22} acids with two double bonds.

The oils of the Delphinidae show some similarity to the head oils of the sperm whale in that they contain considerable amounts of fatty acids of low molecular weight. In the Delphinidae, however, the occurrence of large amounts of iso-

valeric acid (C_5) is a peculiar characteristic. This is one of very few examples of an acid with an odd number of carbon atoms occurring in natural oils. It is present in larger amounts in the head and jaw oils than in the blubber oil. The unsaturated fatty acids of the Delphinidae are unlike those of the Balaenidae or

TABLE V. Weight percentage composition of fatty acids in marine mammalian oils

Division Mammalia Order Cetacea

	Saturated			Unsaturated				
	C_{14}	C_{16}	C_{18}	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}
Family Balaenidae								
Whale oil (a), blubber								
Arctic, Balaena mysticetus	4	10.5	3.5	–	18(2.5)	33(3)	20(7)	11 (8)
Newfoundland, " "	7.5	10	3	1.5	18(2)	44(2.2)	–	16 (8)
Antarctic, " australis	8	12	2	1.5	15(2)	43(2.3)	8(7.5)	10.5(9)
Family Physeteridae								
Antarctic sperm whale, Physeter macrocephalus,								
head*	14	8	2	14(2)	15(2)	17(2)	6.5(2)	–
blubber	5	6.5	–	4(2)	26.5(2)	37(2)	19(2.5)	1(4)

*Head acids also contained 3.5% capric, 16% lauric and 4% lauroleic acids: the blubber acids 1-2% lauric acid.

	Saturated					Unsaturated				
	C_5	C_{12}	C_{14}	C_{16}	C_{18}	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}
Family Delphinidae										
Porpoise, Phocaena communis										
body oil	13.6	3.5*	12.1	4.7	nil	4.7(2)	27.2(2)	16.7(2.8)	10.5(4.8)	7(4.9)
head oil	20.8	4.1	15.8	7.5	0.2	4.6(2)	20.8(2)	15.2(2.6)	9.4(4.5)	1.6(4.7)
jaw oil	25.3	4.6*	28.3	4.1	nil	3.2(2)	20.3(2)	9.3(2.6)	4.9(4.9)	nil
Dolphin, body oil	3.2	1.0	7.2	8.6	0.8	4.7(2)	25.9(2)	24.1(3.3)	18.6(6.5)	5.9(7.6)
head oil	13.9	2.4	12.5	11.6	0.4	2.7(2)	25.4(2)	15.8(2.8)	12.7(5.5)	2.6(7.2)
White whale (Beluga) (e)										
Delphinapterus leucas										
body	4	–	–	28.0	–	–	–	51	–	1.2
head	25.6	–	–	29.1	–	–	30.2	1	–	0.5
jaw	20	–	–	14.1	–	–	–	51.5	–	1.3

*Trace of lauroleic acid.

Physeteridae in that palmitoleic acid predominates. The C_{14} and C_{18} acids are largely monoethylenic but those of the C_{20} and C_{22} series contain more unsaturated members.

(c) GLYCERIDE STRUCTURE

All animal and vegetable fats contain a variety of fatty acids and it is of some interest to consider in what combinations these acids are united with glycerol to form the natural glycerides. Hilditch and Lea (1927) have developed an oxidation method by which the general structure of the mixed saturated-unsaturated glycerides can be determined. This new method has given results that confirm the view that the presence of simple glycerides (i.e. three molecules of a single fatty acid united to a molecule of glycerol) in natural fats is of comparatively rare occurrence and that the fatty acids tend to be distributed as evenly as possible throughout the glyceride molecules. Simple triglycerides, therefore, occur very infrequently in appreciable quantities and then only when one of the component fatty acids is present in a large excess over the others. Vegetable fats and some of the depot fats of terrestrial animals follow this even-distribution law but for the milk fats and the body fats of the ox, sheep and pig there is a greater amount of fully saturated glycerides than would be expected were the fatty acids evenly distributed.

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The oxidation method of Hilditch is suitable for the analysis of fats with a considerable proportion of saturated fatty acids. It is of limited value when applied to marine animal oils. In this case, most of our information concerning glyceride structure comes from actual crystallization of the oils after they have been brominated, as exemplified by the studies of Suzuki and his co-workers (1927 *et seq.*). These investigators have isolated qualitatively a great number of glycerides from marine animal oils. Although the actual composition of some of these glycerides, as isolated, may not be entirely correct, it is significant that in a recent summary only three simple glycerides were listed whereas 24 glycerides with two different fatty acids and 20 with three different fatty acids were noted.

Marine animal oils, therefore, are seen to be complex mixtures of very complex compounds. In addition to possessing a large number of different fatty acids of various degrees of unsaturation, these fatty acids are united to the glycerol in numerous combinations of two and three at a time. The likelihood of *appreciable* amounts of saturated glycerides occurring is therefore very remote. Using two methods of oxidation (permanganate and ozone), W. A. Riddell in these laboratories obtained less than 3 per cent of "saturated" glycerides from pilchard oil. These glycerides, even after vigorous oxidation, still had an iodine value of 12 units.

III. FACTORS THAT INFLUENCE THE COMPOSITION AND QUANTITY OF FATS IN FISH

There are at least four factors that influence the composition and quantity of fats in fish. These are species, food, sexual maturity and temperature of the sea water. Just how far these factors are interrelated is not known with certainty, but it would appear that food at least is to some extent dependent on sea temperature and therefore changes, apparently related to temperatures, may be brought about by the changing nature of the available food. Salinity of the sea water has also been suggested as a factor influencing the composition of fish fats but the data at present available are too few to be conclusive. Certainly, the changes that take place in those fish that make their spawning migration from salt to fresh water are very striking, but this may be entirely a matter of sexual maturity. Similar changes are noted in fish that spawn at sea.

Before considering the above factors in relation to the composition and quantity of fats found in fishes, it might be of value to review briefly a few facts concerning animal fats in general.

Although fat is found in other parts of the body, that stored as a reserve food supply is deposited in the adipose tissue from which it may be drawn as occasion requires. An animal usually deposits fat only when the food eaten exceeds the amount utilized by the body for energy requirements. The nature of the deposited fat depends to a certain extent on the nature of the food eaten. By changing the diet of an animal the nature of the deposited fat can be changed. Corn-fed hogs, for example, produce soft lards due to the high oil content of the diet. Similarly, cattle fed on an oil-cake diet yield softer tallows than those fed on a grass (largely carbohydrate) diet.

The animal body has the ability to modify ingested fats before depositing them in the adipose tissue. When the energy content of the diet is in excess of that required by the animal and the diet also contains an excess of fat, the fat deposited in the body will tend to resemble that ingested. On the other hand, an active animal, fed on a balanced diet, will produce a body fat typical of the species irrespective of the nature of the fat ingested.

Since diet and life habits have a profound effect on the nature of the deposited fats, animals in general tend to form specific fats only in so far as their diet and habits are specific. However, any species lives on a more or less characteristic diet, and the fats formed are, within certain limits, generally characteristic of that species.

Recent work has shown that there is a constant interchange between ingested fat and stored fat. If the ingested fat is of a type similar to that stored, then there will be no change in the composition of the latter. If, however, the ingested fat is of a nature different from that stored, the animal body will endeavour to modify it so as to make it similar to the stored fat. If the foreign fat is present in the diet in small amounts only, the body may be successful in this modifying process, but when fed in large amounts the process of modification breaks down and some of the foreign fat may be deposited unchanged in the adipose tissues.

(a) SPECIES

Undoubtedly one of the most important factors in determining the nature of a fish fat is the species of fish from which it is taken. This may be due to the particular feeding habits of the fish, but superimposed on this is the ability of the fish to modify ingested fats to suit its own needs and, in some measure at least, the extent and nature of this modification is peculiar to the species of fish concerned. In the animal kingdom in general the depot fats are more characteristic of the species than the organ fats (liver, etc.), but it must be remembered that in fish the liver is sometimes the main fat storage depot and this has a profound bearing on the amount and nature of the liver fat. In considering commercial fish oils in relation to species, one must therefore take into account the nature of the chief depots from which the fat was obtained.

The iodine value and refractive index are two analytical characteristics serving as very sensitive indicators of changes in composition of an oil, particularly in regard to its total unsaturation. In general, there is a linear relationship between these two values so that refractive indices can be used to indicate the gross unsaturation. The higher the refractive index, the more unsaturated is the sample. In figure 2 will be found the refractive indices of a number of samples of ten different fish oils plotted as percentage-frequency curves. It will be observed that the refractive indices of each kind of oil fall within fairly well defined limits. These limits are more restricted in some species than in others and, furthermore, oils from a species caught in certain waters may show an average unsaturation different from those of the same species caught in different waters. This is illustrated by the distribution curves of the Atlantic and Pacific halibut liver oils.

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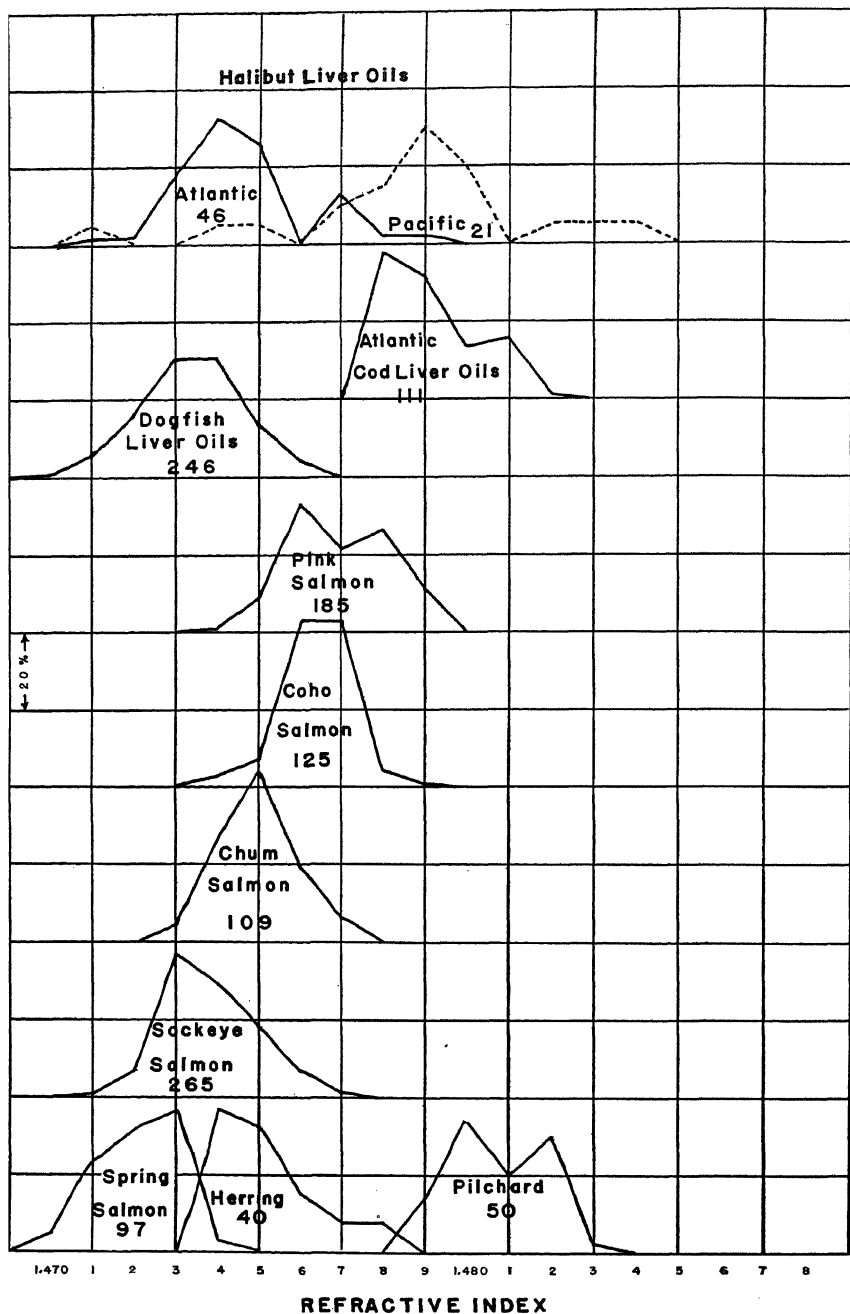
FIGURE 2. Refractive index frequency curves for ten fish oils. The numbers of samples used are given. (Salmon oil data from Harrison *et al*. 1939; cod liver oil from Holmes and Clough

The former are in general less unsaturated than the latter. This fact is amply corroborated by iodine values.

A difference in iodine value or refractive index means a difference in the composition of an oil, but oils with the same iodine value or refractive index do not necessarily have the same composition. For instance, the refractive indices of cod liver oil tend to overlap those of pilchard oil but, as pointed out in a preceding section, these two oils are very different in chemical properties. Usually, however, two oils from the same species of fish, with similar iodine values and refractive indices, will be found to have identical properties and composition.

Even fish in the same genus but of different species tend to form their own characteristic oils. This is illustrated by the Pacific salmon; each species tends to produce a body oil with definite limits of unsaturation as shown in figure 2 and table VI.

TABLE VI. Range of unsaturation of various salmon oils

Kind of salmon		Iodine values		Insol. bromides	
Common name	Scientific name	Lowest	Highest	Lowest	Highest
Red, sockeye or blueback	Oncorhynchus nerka	140.7	148.2	32.6	37.4
Chinook, king or spring	Oncorhynchus tschawytscha	126.6	134.5	23.9	31.1
Medium red, coho or silverside	Oncorhynchus kisutch	152.5	166.4	43.1	59.3
Humpback or pink	Oncorhynchus gorbuscha	153.6		40.2	
Chum or dog	Oncorhynchus keta	133.1	147.8	27.6	35.3

The above data were obtained by Bailey and Johnson (1918) in the examination of a large number of cans of salmon. They do not represent the actual limits found for similar oils by other workers, but, since they were obtained on the canned product and therefore from one fat depot only, the data can be interpreted as showing a distinct trend towards a characteristic grouping of the oils.

Other analytical features of fish oils may show this tendency towards species characterization. For instance, the content of unsaponifiable matter, and in some cases the actual composition of the unsaponifiable matter, inclines to be constant. However, there are more exceptions for this than for unsaturation. For instance, as noted in a previous section, the liver oils of closely related species of sharks may have contents of unsaponifiable matter ranging from less than 10 to over 80 per cent. Nevertheless, variation in any one species is much less than this. In general, oils from muscle depots have a lower and more constant quantity of unsaponifiable matter than those from internal organs such as the liver, even though the latter may be the main fat storage depot.

The ability of fish to produce depot fats with characteristics peculiar to their species must mean that they can either modify their ingested fats or select their diet, or possibly do both of these. Lovern's work on the fats of the tunny is

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particularly interesting in this regard, as the tunny is a fish that has a body temperature about 3°C. higher than its surroundings. In examining the fats from the pyloric caeca, heart, flesh, spleen and liver, Lovern found for it, in comparison with the majority of marine species, the following peculiarities: "For the saturated acids, high stearic and to a less extent high palmitic acid contents, and in three cases the absence of myristic acid; for the unsaturated acids, low palmitoleic acid content and entire lack of myristoleic acid (C_{14}) normally present in traces in aquatic plants." In other words, there is a shift from the lower fatty acids to the higher (and more saturated) and it would appear that this shift is related to the higher body temperature of the tunny over that of other fish.

The mechanism of the formation of the higher amounts of stearic and palmitic acids is apparently that of hydrogenation of the unsaturated members of the C_{18} and C_{16} series to the saturated forms, since in the oils from the five depots listed above, as the stearic acid content increases there is a progressive decrease in the unsaturation of the C_{18} unsaturated acids—the former is being produced at the expense of the latter. The high proportion of stearic acid present is not due to the food because the fat of the pyloric caeca (consisting largely of food fat) has the *lowest* stearic acid content. To some extent, therefore, fish can control the saturated fatty acids in their depot fats.

The questions now remaining to be considered are: Can fish desaturate fatty acids to suit their particular needs, and can they synthesize fatty acids of various carbon contents from sources other than fat? The answer to both these questions, at least in the species investigated, appears to be in the affirmative. Lovern investigated the fatty components of a fresh water carp that was fed entirely on grasses, and another that was fed entirely on mud. In comparing the compositions of the fat of the grasses and of the fat of the mud with those of the two kinds of carp, he concluded that "the evidence taken as a whole indicates that these fish are able to synthesize fat of the desired type from carbohydrate or other sources." In this case fat of the desired type included the formation of C_{22} acids (lacking in the ingested fats) and a general increase in the unsaturation. Other evidence, of a more indirect nature, points to the ability of fish to desaturate fatty acids and/or to deposit them selectively. Lovern finds that the fat from the eggs of Atlantic salmon are more highly unsaturated than the fat in the storage depots from which they are drawn. In these laboratories Harding has found the same to hold for Pacific coast coho salmon (see Section 10) and Bailey (1934) has shown that in Pacific coast salmon, in general, the liver fat is very much more unsaturated than the muscle depot fat.

Finally, attention must be drawn to the fact that, contrary to the view held in regard to mammals, in fish the liver does not in all cases appear to be the site of desaturation. In fish livers which are not fat storage depots, the fat is usually very highly unsaturated (i.e. salmon), but in other livers which are one, if not the main, storage depot, the liver oil is usually much less saturated than the body oil. There is some evidence that saturation and desaturation take place at the site of storage and it has been postulated that the mechanism consists in a reversible

enzymic system which acts to maintain a proper balance between saturated and unsaturated fatty acids.

(b) DIET

The food of all marine animals is, in the last analysis, of vegetable origin—mainly phytoplankton which floats and lives in the upper strata of the sea where there is enough light to permit the utilization of carbon dioxide in the synthesis of carbohydrate, protein and fat. This phytoplankton forms the food of plankton Crustacea and other zooplankton; these in turn constitute the main diet of the smaller fishes and also of some of the larger marine mammals such as the whales. The larger carnivorous fish feed on the smaller fish and the chain is complete. Life in the sea, as on land, is dependent on vegetable matter for its existence and it is of some interest to trace the fats characteristic of marine organisms through these sequences. The data are far from complete, but even so, some general conclusions can be arrived at with respect to the influence of diet on the type and quantity of fat in fishes.

In 1925, Tsujimoto showed that marine algal plants contain very small quantities of highly unsaturated fatty acids. Collin *et al.* (1934), found that fatty acids from mixed phytoplankton gave only slight traces of these characteristic highly unsaturated acids. Lovern examined the fats of green, brown and red marine algae and of a single species of diatom. The green and brown algae and the marine diatom all had fats resembling those of fresh water fish more than those of marine fish (fresh water fish oils have greater amounts of unsaturated C_{16} and C_{18} than marine fish oils but less unsaturated C_{20} and C_{22} acids—Lovern), but the red algal fat was similar to the latter. However, the plankton Crustacea live on small floating algae and diatoms, and the latter contain a fat with a low content of unsaturated C_{20} fatty acids and entirely lacking unsaturated C_{22} acids. The bulk of the evidence available, however, indicates that the plankton Crustacea that feed on diatoms and other marine phytoplankton, have a fat that approximates the composition of marine fish fats in having important amounts of C_{20} and C_{22} unsaturated acids, and it would appear, therefore, that these Crustacea are able to modify considerably the fat of the ingested diatom food before storing it. This seems to be equally true of the larger and the smaller forms of Crustacea. Fish that feed on Crustacea, therefore, have accessible to them in their diets fats containing unsaturated C_{20} and C_{22} acids, but those fish that feed on diatoms would lack C_{22} acids in their diet, at least in important amounts.

Before considering the diets of some of our important fishes, it is worth while at this time to summarize an interesting experiment made by Lovern on the controlled feeding of fish. Two lots of eels were fed separately on a low and a high fat diet. On the diet low in fat (1.1%) the ingested fat had no detectable effect on the depot fat of the eels. On the diet high in fat (20.7%) the depot fat of the eel was appreciably modified. The ingested fat was apparently laid down with the relative proportions of the acids in the various carbon series unchanged, but the degree of unsaturation in each series was altered, considerable saturation

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of the acids having taken place. The eel, therefore, seems to be able to bring about a hydrogenation of its ingested fat.

Apart from the controlled experiment just described, there are no accurate data relating the composition of the fat actually ingested by fish to that of the depot fat. However, the information that is available supports the evidence for considerable modification of the ingested fat by the species concerned. Two examples of Pacific coast fishes, the feeding habits of which are fairly well known, will further illustrate this point. The herring and the pilchard are closely related fishes, but their diets are considerably different. The chief food of the adult herring consists of small crustaceans, "*Calanus* being most important in the spring and *Euphausia* during the rest of the year" (Wailes 1935). On the other hand, Hart (1937) states that "Extensive food-studies on the British Columbia pilchards show that the adults depend chiefly on these diatoms as food during the summer, although the copepods remain an important secondary food." Herring, when caught for commercial purposes, are rarely found feeding, but the pilchards are caught during the active feeding period. Now there is a distinct difference in the nature of the oils from these two fishes. Herring oil varies in iodine value from about 120 to 150, pilchard oil from 170 to 190. The fat of crustaceans, however, has a much higher iodine value than that of diatoms (calculated from Lovern's data, iodine values of fatty acids of a typical copepod and diatom are 212 and 156 respectively). Consequently, herring appear to be able to saturate and pilchards to desaturate their respective ingested fat. A careful study is now being made of the relation between the nature of the fat in the stomach contents and the depot fats of these two fishes, and the results should throw some light on the relationship of food to character of deposited fat.

Finally, it hardly need be mentioned that the food intake of fish controls their fat content. In the early summer pilchards arrive in British Columbia waters and commence feeding. They feed continuously for about three months during which time their oil content increases almost a hundredfold, and the oil yields in reduction plants show almost daily increases throughout the fishing season. Purse-seined herring are not in the process of feeding and oil yields of herring reduction plants show gradual declines until the fish disappear. Data accumulated by various investigators throughout the world show that, in general, as fish feed they fatten up in preparation for the spawning period during which time their reserve fat supply forms their only source of energy.

(c) SEXUAL MATURITY

In most fishes the spawning period has a profound effect on the stored fat. Usually feeding ceases some time prior to spawning and this, plus the great drain on reserve food supply occasioned by the rapidly maturing sexual organs, causes a severe depletion of fat reserves. This is true both of fish that store their fat in the muscle tissue, as in the salmon and herring, and also of those that store it in the liver, as in the case of the cod. In some fishes, however, where spawning appears to take place at any time throughout the year, there does not appear to

be such a depletion. This is exemplified by such fish as the dogfish, the young of which are born alive and whose liver fat does not seem to vary extensively with sexual condition.

The three fishes mentioned above represent three distinct types as far as spawning habits are concerned. Herring spawn in salt water; salmon ascend rivers and spawn in fresh water; dogfish have no definite spawning period and give birth to fully developed offspring. It is interesting, therefore, to follow the changes in the fat of these fish during the reproductive cycle.

The changes in the fat during the spawning migration of Pacific salmon is amply demonstrated by the work of Greene (1913) on king or spring salmon, and of Davidson and Shostrum (1936) on pink salmon. Greene emphasized the following facts regarding the spawning migration of the king salmon. The king salmon fasts completely during its entire journey from the sea through the tidal waters and up the rivers to the spawning grounds. Fat is the predominant and immediate source of energy during this period, and is stored in the body during the stage of feeding and growth, reaching a maximum just prior to the spawning migration. The chief storage tissues are the muscle and interconnective tissue, the former being the more important. The muscle tissue is of two types, the superficial dark muscle and the deep pink muscle. The dark muscle has fat between the muscle fibres but is characterized chiefly by enormous loading of fat within the muscle fibres themselves. On the other hand the pink muscle fat is nearly entirely intermuscular, very little appearing within the muscle fibres. The fat content of the dark muscle always exceeds that of the pink muscle but the fat of both muscle tissues gradually decreases during the spawning migration, never wholly disappearing, however, even in spawned, dying salmon.

In a later paper Greene (1919) showed the quantitative loss of fat by king salmon during their spawning migration by analyzing a number of fish at various distances up the stream in which the fish were migrating. His results were as follows: Tide-water, 15.5% fat; 130 miles, 16.5%; 210 miles, 15.5%; 700 miles, 10.4%, and on the spawning grounds, 2.2%. There was an apparent loss of over 85% of the stored fat from the time the fish left the sea until they had spawned.

Much the same conditions were found in pink salmon by Davidson and Shostrum. They stress three factors that influence the fat content of pink salmon at the time of capture, namely (1) the amount of fat stored at the beginning of their migration from the feeding grounds in the sea, (2) the amount of stored fat that they utilize for maintenance before being captured and (3) the amount of stored fat utilized for sexual development. The farther the fish have to travel to reach the spawning stream the more energy is expended and also the greater the sexual maturity. Some idea of the effect of these factors is given by the curves in figure 3. These represent the fat content of male and female fish in a daily sample of ten pink salmon entering their spawning stream from the beginning to the end of the spawning migration. In both the male and female fish there is a distinct trend towards depletion of fat, particularly in the latter part of the migration period. In regard to these data Davidson and Shostrum say:

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"The gradual increase in the fat content of the salmon during the first ten days of the migration may be due to a greater growth of the incoming salmon from the standpoint of storage of fat in their bodies. Were it not for the fact that sexual development begins to show its effects on the composition of the salmon that remain longer on the feeding grounds, the fat content of the incoming salmon would no doubt first rise and then fluctuate about a maximum value during the remainder of the migration. However, the drain upon the energy reserves of the salmon due to sexual development so shows its effects on the fat content of the incoming salmon and the trend in this constituent begins to fall at an ever-increasing rate."

Lovern has studied the changes in composition of the fat of salmon and of the eggs during the spawning migration. In the case of the male salmon the stored fat was withdrawn selectively, as there was a loss of the fatty acids of smaller molecular weight, resulting in a rise of the C_{22} acids in the depots of the starving fish. In females the same selectivity appeared but was not so evident, as C_{22}
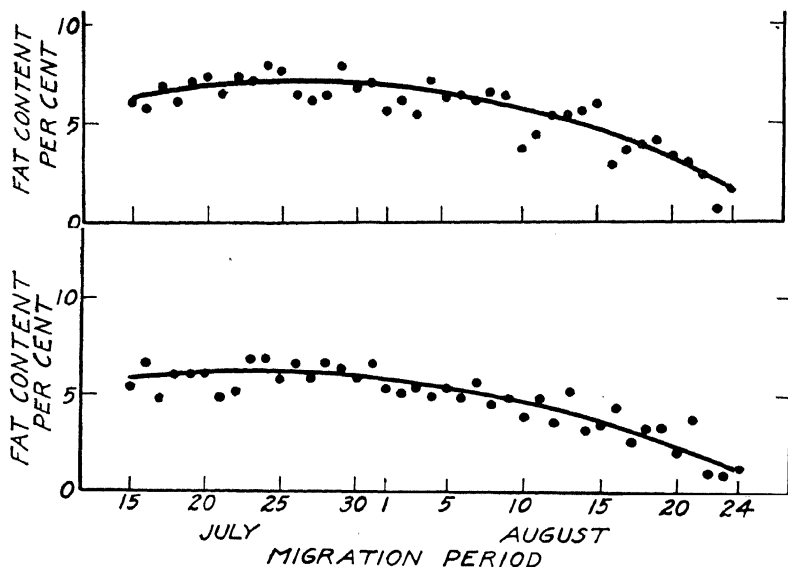
FIGURE 3. Change in fat content of pink salmon during 1933 spawning migration at Olive cove, Alaska (Davidson and Shostrum 1936). Males,—top; females,—bottom.

acids decreased in the storage fat instead of increasing. In the eggs, during all stages of development the degree of unsaturation of both the C_{20} and C_{22} acids is greater than in the depot fats. Also, as ripening proceeds, there is a marked rise in the proportion of C_{18} acids and at the same time the mean unsaturation of this group decreases. Lovern states: "In contrast to the C_{22} acids, the preferential translocation of C_{18} acids to the ova does not affect the depot fat composition, and the selective process must operate after the fat has been mobilized." In other words, the depot fats of spawning salmon undergo a slight change in composition in that their content of C_{22} acids varies with spawning. The difference in com-

position of the egg fat arises after the parent fat has been withdrawn from the depots, most probably within the maturing eggs themselves.

In regard to Pacific coast herring there are no analytical data available to show the change either in amount or in composition of fat during the spawning period. However, as far as the amount of fat is concerned no analyses are required; a glance at the weekly yields of oil from plants producing meal and oil from herring shows a definite depletion in oil as the spawning period approaches. Herring are taken commercially on the Pacific coast between the feeding and spawning periods. Such fish very rarely contain feed. When they first appear in schools large enough to seine, they yield about 18 to 20 gallons per ton of fish.
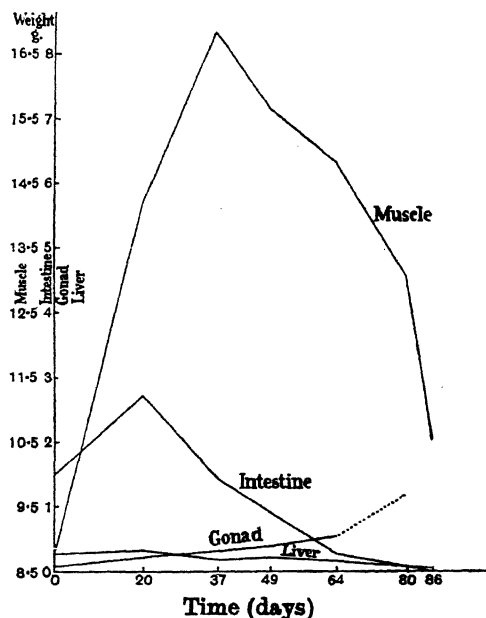
FIGURE 4. Variation in weight of fatty acids in tissues of average herring during maturation period (Channon and Saby 1932).

This yield decreases to below ten gallons per ton prior to the fish disappearing to spawn. An examination of a few spawned herring in these laboratories showed them to be very lean and relatively non-oily.

Channon and Saby (1932) have followed the weight of fatty acids in the muscle, intestine, gonads and liver of herring from the Port Erin fishing grounds during a period of 86 days. Their results are shown in figure 4. They "may be taken as an approximate indication of the changes which occur in a 3-year old herring during the period of active growth of the gonads from an initial weight of 0.8 grams to a final weight of 39 grams when spawning occurs." The liver fatty

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acids show a slight increase during the first three weeks and after that steadily decrease until after spawning there is practically none left. The intestinal fatty acids also increase up to the third week and thereafter decrease. The fatty acids of the muscle, however, increase for a longer time (approximately five weeks) and reach their maximum about the half-way stage in the maturation process. They then decrease at about the same rate until after spawning. The gonad fat increases steadily up to the time of spawning. As far as commercial fishing is concerned the variation in the muscle fat is, of course, the most important, there being more fat in the muscle than in all the other organs combined. The sharp decline in muscle fat after the fish have stopped feeding and prior to actual spawning is in excellent agreement with the findings of operators on the Pacific coast. The marked rise in fat content during the feeding period would suggest that, if operation on summer herring were possible, greater oil yields would be obtained than on winter herring.

TABLE VII. Seasonal changes in herring fat (Lovern)

Month caught	% Fat	Iodine value of fat	Saturated C_{14}	C_{16}	C_{18}	Unsaturated C_{14}	C_{16}	C_{18}	C_{20}	C_{22}
April	8.2	115.5	8.0	15.7	0.2	–	4.6 (-2.6H)	22.2 (-2.9H)	22.0 (-3.9H)	27.3 (-4.2H)
June	10.7	144.2	7.5	16.7	T	0.6	7.5 (-2.7H)	21.1 (-3.3H)	27.3 (-4.8H)	19.5 (-5.7H)
June	15.7	154.3	7.5	12.8	0.1	0.3	7.0 (-3.0H)	21.1 (-4.8H)	30.0 (-5.2H)	21.2 (-4.8H)
July	20.7	152.5	8.3	12.1	0.3	0.5	6.4 (-3.4H)	21.0 (-4.5H)	28.3 (-5.5H)	23.1 (-4.6H)
October	18.8	138.6	7.3	13.0	T	0.8	4.9 (-2.7H)	20.7 (-4.2H)	30.1 (-4.6H)	23.2 (-4.3H)
October	12.0	129.9	6.6	13.7	0.5	0.2	4.9 (-2.8H)	16.3 (-3.6H)	28.7 (-4.4H)	29.1 (-4.1H)
April (immature fish)	4.6	147.9	5.8	12.4	0.6	–	4.7 (-3.0H)	17.8 (-3.9H)	31.1 (-4.3H)	27.6 (-4.8H)

Lovern has studied the seasonal changes in composition of Atlantic herring fat and since his results, in general, probably apply to the Pacific herring the complete data are presented in table VII.

The gross unsaturation rises and falls with increasing and decreasing fat content and several interesting changes in composition also occur. Regarding all the herring oils analysed, Lovern observes that there appears to be a higher proportion of C_{22} acids than usually occurs in fish oils. The chief characteristics of herring oils, however, are the abnormally high unsaturation of the C_{16} acids and unusually low unsaturation of the C_{22} acids. In most samples the C_{18} acids were particularly unsaturated and the C_{20} acids more saturated than in the average fish fat.

The seasonal variation in the proportions of the different acids appears in some cases to be significant. Judged from the above data the proportion of C_{22} acids is greatest in fish with low oil content. The proportion of C_{20} acids also

increases with the oil content, but does not decrease in the October spawned fish, and in the immature fish (sample 7) it reaches the highest value of all. The amounts of C_{16} and C_{18} acids do not vary significantly. As regards unsaturation all acids become more unsaturated during the intensive feeding period, the least increase being in the C_{16} acids. In the case of the C_{22} and C_{18} acids the maximum unsaturation is reached earlier than the maximum fat content.

TABLE VIII. Effect of sexual condition and size of dogfish on liver oil content

Description of fish	Sample (no.)	Oil in liver (mean %)	Standard deviation
Non-pregnant females............	144	71.5	4.82
Pregnant females...............	44	67.0	8.70
Males and non-pregnant females:			
65–71 cm.		68.3	5.60
72–78 "	21	70.1	5.31
79–85 "	46	71.6	4.65
86–92 "	51	72.1	4.75
93–99 "	40	74.0	4.18
100–107 "	33	74.2	3.80

In Lovern's opinion the herring prefers a depot fat with comparatively saturated C_{20} and C_{22} acids and, consequently, these acids in the diet are partially hydrogenated during deposition. A major ingredient in the diet of the herring is the crustacean *Calanus finmarchicus*, which is rich in fat. This fat is highly unsaturated, as observed earlier, and during rapid feeding it is likely that the hydrogenation mechanism of the herring proves temporarily inadequate; hence the rise in total unsaturation of all the component acids. When the hydrogenation process is able to cope with the ingested fats there is a selective action in favour of the C_{22} acids. The C_{20} acids appear to be continuously hydrogenated and the C_{18} acids also, but to a lesser degree. The unsaturation of the C_{16} acids in herring is higher than it is in the crustacean fat, and Lovern believes that dehydrogenation of the C_{16} acids goes on during intensive feeding at the same time as the hydrogenation of the higher acids.

This interesting work of Lovern's is extremely important, furnishing, as it does, a clue to the seasonal changes in the nature of the oil in one of our most important sources of commercial fish oil.

Unlike salmon and herring, dogfish do not show a great variation in the oil content of their chief fat storage depot. Table VIII, taken from a paper by L. I. Pugsley (1939), indicates that as the fish become larger the oil content of their livers increases. In the case of mature females there appears to be a slight tendency for the oil content of the livers to recede during pregnancy. Since there is no definite spawning period for these fish, it is not possible to foretell what oil yields might be expected from the livers. A notable exception to this statement, and one not apparently related to sexual condition, is the oil content of the so-

called "mottled" livers. The great majority of dogfish and other shark livers are of a putty-grey colour and these usually contain from 60 to 80 per cent oil. About 2 per cent of the livers so far examined, however, are of a dark colour with mottled patches. These livers never contain more than 40 per cent oil and, peculiarly enough, the vitamin A content of the oil is always a great deal higher than in that from the ordinary grey livers. So far no explanation has been found for this phenomenon.

(d) TEMPERATURE

The effect of climate (or temperature) on the unsaturation of plant fats has been well studied. In an excellent review of the literature of this subject, Ivanow in Hefter-Schönfeld (1936) gives ample data to show that the colder the climate the more unsaturated will be the fat of any particular plant. In applying the "climate theory" to animal fats, Ivanow writes:

'The evolution of the climate theory is based on investigations of plant fats. Its significance in animal fats is unquestionable. The terminology of W. Halden of "poikilothermic "animals with changing body temperatures and "homoiothermic" animals with higher and constant body temperatures fits in closely with the climate theory. In this case warm-blooded animals of constant high temperature have a low content of unsaturated fatty acids, with consequently a low iodine value (circa 100); the changing body temperature of poikilothermic animals tends to form unsaturated fatty acids with 2 and more double bonds and higher iodine values. Consistent with this view is the typical formation of clupanodonic acid with many (four) double bonds and even acetylenic bonds by the poikilothermic fish and animals of the Arctic ocean.'

The above views suggest that temperature may play an important role in determining the unsaturation of a fish fat. In considering the effects of temperature on the unsaturation and amount of oil or fat in the depots of fishes, it must be borne in mind that any relationship deduced from existing data will not entirely rule out the possibility of the food of the fish playing an important intermediate link. The only exceptions to this statement are the data of Lovern on the controlled feeding experiments where differences in food due to differences in temperature were eliminated. Lovern states: ". . . temperature has a direct effect on the composition of the (deposited) fat. Lower temperatures lead to more unsaturated fats and higher temperatures to increased saturation. The effect is a relatively small one and in natural conditions cannot be important." The temperatures which Lovern compared were 14 and 23°C. It must be remembered, however, that Lovern's experiments were made with but one kind of fish and it is possible that this fish (the eel) may not possess a very efficient mechanism for modifying the unsaturation of its ingested fats. Furthermore, these experiments do not rule out the possibility, noted above, that temperature may play an important role through the medium of the food. The following data are recorded, however, simply as cases where there is an apparent relationship between temperature and unsaturation.

Some time ago A. R. Lange (1926) published some analytical data on commercial fish oils and made the following statement: "As a rule, fish oils made from fish caught in northern waters yield less stearin (stearine) than oils made

from southern-water fish.   But both northern and southern fish oils are met with
with varying iodine numbers." Brocklesby and Bailey (1932) reported that for the
free oil from canned sockeye and pink salmon there was a distinct increase in
unsaturation the farther north the fish were caught. The data which are pre-
sented in table IX were obtained by combining the free oil from 24 one-pound
cans of salmon. These cans represented a selection of a day's pack in one cannery.
The samples were all obtained during the same season.

TABLE IX.   Unsaturation of some canned salmon oils packed in three different areas

| Kind of salmon | Place at which canned | Iodine value | Refractive index at 25°C. | Brominated fatty acids insoluble in | |
				ether (%)	chloroform (%)
Sockeye........	Fraser river......	135.2	1.4760	28.9	22.8
	Rivers inlet......	143.3	1.4771	32.0	26.7
	Skeena river.....	151.5	1.4775	36.5	28.2
Pink...........	Fraser river......	157.4	1.4780	40.3	31.0
	Johnstone straits.	160.7	1.4784	42.6	31.8
	Butedale........	161.3	1.4790	43.2	32.3

These data, although showing a distinct trend towards a higher unsaturation
in the more northerly fish, unfortunately cannot be directly correlated with
temperatures as the latter are not available for the above areas during the time
the fish were caught.   Furthermore, they may represent changes in the oil due to
varying sexual maturity as, in general, the farther south the fish are caught,
the longer they have been on their migration towards their particular spawning
stream.

Somewhat more definite data are those relating to the unsaturation of pil-
chard and sardine oils of the Pacific coast.   The writer and his associates have
had the opportunity of examining a series of oils starting at the beginning of the
fishing season in British Columbia when the pilchards (or sardines) are feeding,
and subsequent samples as the fish migrate down the California coast where they
are taken commercially during the fall and winter months.   The data, which are
too numerous to report in detail, show that there is a very distinct trend of
increasing unsaturation in the fish as they progress farther south.   The maximum
difference between the northern-caught and southern-caught fish was something
over 12 units in iodine value.   In the fishing season in British Columbia, during
which time the fish feed, the writer has noticed an occasional tendency towards
increased unsaturation as the season progresses; that is, as the fat content in-
creases.   As the fish migrate south they are presumably not feeding but the mean
temperature of the fishing grounds off the California coast during the fishing
season is from 2 to 3 degrees C. lower than that obtaining during the fishing

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season off the British Columbia coast. Thus the increasing unsaturation is in keeping with the decreasing temperature. However, even here no definite conclusions can be drawn, as the age compositions of the fish in the two areas differ from each other and also in themselves during the season, and this may be a factor contributing to the change in unsaturation.

It must be concluded, therefore, that, whilst there are indications that unsaturation increases with decrease in temperature, further data must be available before such a correlation can be said to be definite.

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SECTION 3. VITAMINS AND OTHER NON-FAT
COMPONENTS OF MARINE ANIMAL OILS

A marine animal oil is usually thought of as consisting chiefly of true oily or fatty substances, i.e. glycerides of fatty acids. This conception holds for the majority of whole body oils and many liver oils. But oils from certain shark livers have been reported to consist of materials of which 90 per cent are not true fats. The several types of such materials are collectively classed as the *unsaponifiable matter* of the oil, or simply "unsaponifiables", defined for analytical purposes as consisting of "that material present in oils and fats which, after saponification of the oil or fat by caustic alkali and extraction by the solvent specified (usually ethyl ether), remains non-volatile on drying at 80°C.(176°F.)." (Cocks 1933). In view of their abundance in some oils, a further consideration of their properties is warranted.

Substances that can be present in a crude marine animal oil include: Group A —fatty acid esters of (1) glycerol, (2) sterols, (3) glycerol ethers, (4) phospho-lipides, (5) vitamins, and (6) pigments; Group B—(7) waxes (fatty acid esters of fatty alcohols), (8) pigments, and (9) dissolved nitrogenous materials; Group C —(10) hydrocarbons (including some pigments), and (11) fatty alcohols. In addi-tion, there may be present some uncombined fatty acids, glycerol and other components of the esters in group A, either occurring naturally or resulting from hydrolysis of their esters during the separation of the oil from the tissues. Sus-pended water and nitrogenous materials sometimes present are classed as impuri-ties that should not occur in a high-grade oil; their removal, if present, is discussed elsewhere. The significance of the foregoing definition of the term unsapon-ifiable matter, as applied to the various substances mentioned above, may be gathered from a consideration of their behaviour upon the application of the ordinary saponifying procedure used for the determination of such unsaponifiables.

GROUP A

All six types of fatty acid esters in this group are saponifiable. The fatty acid portions combine with the saponifying alkali to yield fatty acid salts (soaps) which are soluble in the saponifying medium but insoluble in ethyl ether. Of the residual components with which the fatty acids were originally combined, the glycerol formed by the saponification of the true fats (1) is soluble in water and insoluble in ethyl ether. The chief pigment (astacin, page 78) formed from (6) combines with the alkali and is also thus rendered insoluble in ethyl ether. The components resulting from the saponification of the phospholipides (4) are much more soluble in water than in ether, and probably do not remain in the unsaponifiable portion to any great extent. The other residual components formed by the saponification of (2), (3) and (5), namely, sterols, glycerol ethers,

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and vitamins A and D, are insoluble in water but soluble in ethyl ether and therefore by definition are classed as unsaponifiables.

GROUP B

True waxes (7) occurring in marine oils require for their saponification more energetic treatment than is ordinarily employed in the estimation or separation of unsaponifiables in such oils. If saponified, the fatty acid portions form soaps and the residual fatty alcohols, being soluble in ether, remain as unsaponifiables. If not saponified, the wax as a whole behaves as an ether-soluble unsaponifiable. The pigments (8) in this group (e.g. fucoxanthin, xanthophyll), although they do not yield fatty acid soaps, may be altered during saponification, but the products form ether-soluble unsaponifiables. The variety and complexity of the possible dissolved nitrogenous materials (9) render it difficult to state their exact fate during saponification; the unaffected substances and those altered by the process probably divide themselves between the soaps and the unsaponifiables from other materials. These nitrogenous substances, strictly to be considered as impurities, should not be present in a high-grade oil in more than minute amounts, and their disposition is of little consequence.

GROUP C

The hydrocarbons (10) (including the pigment carotene) and the fatty alcohols (11) are unaffected by the saponification process and being soluble in ether, they are the best examples of true unsaponifiables in marine animal oils.

Therefore, according to the definition given, the unsaponifiable matter of marine animal oils contains all the components present after saponification with the exception of the soaps, glycerol, water, phospholipide radicals, suspended solids, and the insignificant amounts of the pigment astacin (6) and dissolved nitrogenous materials (9) that may be present in some oils. This holds whether these unsaponifiable substances existed naturally in the oil or were formed by partial hydrolysis during its separation.

These unsaponifiable materials are described more fully in the parts which follow: (I—vitamins, II—pigments, and III,—other non-fat components).

I. VITAMINS

Although the bulk of the dietary requirements of the animal organism is provided by the three foodstuffs—fat, carbohydrate and protein, various other substances are necessary for the maintenance of life and health and the proper development of the young animal. These materials include essential mineral salts and a group of organic compounds known as vitamins. While the latter need only be supplied in very small amounts, a deficiency in them results in retarded growth and bodily disorders, and a severe or prolonged deficiency may ultimately cause death.

Some of the vitamins are soluble in fats and some in water. The two principal members of the fat-soluble group, vitamins A and D, are widely distributed in fish and fish liver oils, and for that reason their properties are discussed here in some detail.

(a) PROPERTIES OF VITAMIN A

(i) PHYSIOLOGICAL PROPERTIES

It has been shown that vitamin A is essential to life and health in mammals, birds and reptiles, but its function in fishes has not been definitely established. The first characteristic symptom of a dietary deficiency of this vitamin in man is usually night blindness, failure of the eyes to become adapted to vision in dim light. In the next stage the sweat glands dry up, and the skin becomes dry and scaly. This scaly condition of the skin, which eventually extends to much of the epithelial tissue of the body, leads to many local infections, since the minute pockets which are formed by the roughening of the surface are excellent breeding places for bacteria. Here again the eyes are involved. The cornea and conjunctiva are among the first places in the body to be infected; the cornea soon becomes opaque, and, unless the condition is checked in the early stages, permanent blindness results. The mouth is another common site of infection, ulcers forming on the gums and on the lips.

Vitamin A has a marked effect in reducing susceptibility to colds and other respiratory infections. For a time it was thought that it was specific in checking such infections, but it is now recognized that the actual reason for its efficacy lies in maintenance of the epithelia of the respiratory tract in a normal healthy state. In cases of vitamin A deficiency these membranes are quickly affected, becoming dried up in the manner already described, and bacteria, entering with the inspired air, can more easily attack them.

The nervous system is also affected by a deficiency of vitamin A. As early as 1914 Hart and McCollum observed that pigs maintained on certain basal experimental rations developed symptoms of incoördination and a staggering gait. In 1916 Hart, Miller and McCollum reported that these symptoms were due to degenerative changes in the nervous system of the animals, caused in part by a dietary deficiency of vitamin A. Hughes and his co-workers in 1928 and 1929 reported extended observations on the effects of vitamin A deficiency on pigs, chicks and cows, in all of which symptoms of incoördination were seen. They found that these symptoms could be correlated with degeneration of the nerve bundles in the spinal cord. Symptoms of a similar nature have been observed in human patients suffering from vitamin A deficiency. Disturbances of the sensory nerves have also been reported.

In addition to the effects already discussed, vitamin A is essential for growth. This was one of its earliest recognized functions, and is still the basis of the bioassay method for the determination of vitamin A potencies. This growth effect is probably not specific, since growth may cease and decline whenever the growing organism is not functioning properly in all its parts, or when it is not supplied with the necessary structural materials.

Finally, it may be mentioned that an adequate supply of vitamin A is absolutely necessary for reproduction and for successful lactation.

One of the characteristic properties of vitamin A is its solubility in oils and solvents. This can be understood from an examination of the structure of molecule, which is largely hydrocarbon.

$$
\begin{array}{c}
CH_3 \quad CH_3 \\
\diagdown \diagup \\
C \\
\diagup \diagdown \\
H_2C \qquad C-CH=CH-C=CH-CH=CH-C=CH-CH_2OH \\
\mid \qquad \parallel \qquad\qquad\qquad CH_3 \qquad\qquad\qquad\qquad CH_3 \\
H_2C \qquad C-CH_3 \\
\diagdown \diagup \\
CH_2
\end{array}
$$
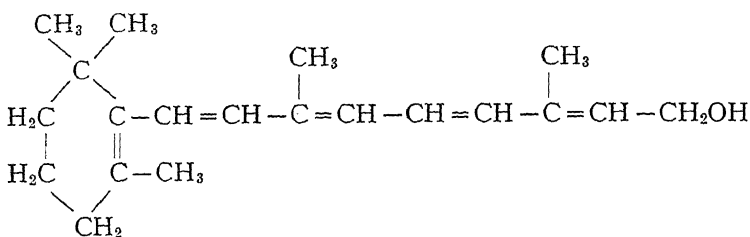
At least part of the vitamin A in the natural materials in which it occurs is he form of esters. The work of Reti (1935) suggested that all the vitamin A ish liver oils is esterified with fatty acids, while according to Tischer (1938) t of this vitamin in Norwegian cod liver oil is free and part is esterified with mitic acid. There is some evidence that the biological value of the esterified n is greater than that of the free alcohol (Moll and Reid 1939).

As far as is known at present, no animal organism has the ability to synthesize vitamin A n simpler materials. It appears to have its origin in plants, where it is formed not as the ımin itself, but as the pigment carotene. Fishes, birds and mammals are able to convert ɔtene into vitamin A, so that a supply of either form in their food can meet their physiological uirements. Carotene was first isolated from carrot roots, but it is of fairly wide distribution ıature, its commonest occurrence being in the leaves of plants, where, however, its colour is sked by the green of the chlorophyll. It is found in the minute floating plants of the sea, the ytoplankton. The latter constitutes the food of many varieties of fish, which assimilate the ·otene, convert it to vitamin A, and store it in their livers, passing it on in turn to the carniv- ɔus fish which feed on them.

Vitamin A is inactivated by light, by oxidation and by the action of various agents. While ultraviolet light is more destructive than ordinary light, ex- ɔsure of an oil containing vitamin A in a clear glass container to sunlight, results a gradual loss of potency, possibly through the action of the sun's ultraviolet ιys. Norris (1931) has drawn attention to the fact that misleading results ιay be obtained when irradiated oils are assayed for vitamin A potency by the ιtimony trichloride colorimetric method. Irradiated oils which are almost ιactive in feeding experiments show 50 to 75 per cent of their original vitamin A otency if tested colorimetrically.

The effects of heat and oxidation on vitamin A have been the subject of ιany investigations, since the importance of accurate information concerning he possible losses during the preparation and storage of oils containing it has ɔng been recognized. Vitamin A is easily destroyed by oxidation but is rela- ively stable to heat in the absence of air or other oxidizing agents. This was irst shown definitely by the work of Hopkins (1920). In one of his experiments wo carefully balanced groups of rats, of ten animals each, were fed a diet of

which butter, the only source of vitamin A, constituted 15 per cent in all cases. One group of the animals received butter previously heated to 120°C. for four hours in an autoclave in which the air was entirely displaced by steam. The other group was given the same butter which had been heated to the same temperature for four hours, but in an oil bath and with simultaneous aeration. The rats of the first group grew normally for the duration of the experiment (70 days), while those of the second group all lost weight and developed xerophthalmia. Wokes and Willimott (1927) made a quantitative study of the oxidative destruction of the vitamin A in cod liver oil. They bubbled air through the oil heated in tubes to various temperatures, and followed the decrease in vitamin A potency by means of the antimony trichloride test. The time required for complete destruction by this means was 105 minutes at 88°C., 75 minutes at 98°, 50 minutes at 108°, 35 minutes at 118°, and 30 minutes at 125°. In similar tubes of oil which were loosely plugged with cotton wool and which were not aerated during heating, the destruction was much slower. Curves are given in their paper showing the course of destruction of the vitamin at each temperature and under each set of conditions described above.

Destruction of vitamin A by oxidation can take place even at ordinary room temperatures, although not so rapidly as at higher temperatures. Thus Drummond, Zilva and Coward (1924) found that a number of samples of cod liver oil stored in partially filled bottles at room temperatures for two years lost a considerable proportion, yet not all, of their vitamin A potency. Loss of vitamin A during storage takes place more rapidly when the oil or concentrate containing it is mixed with finely divided solids. This is probably attributable in most cases to the increased surface of oil exposed to the air when incorporated with such materials. In some instances, however, substances naturally occurring in seeds may have specific effects on the oxidation of vitamin A. While this will also be discussed in the section of this Bulletin dealing with rancidity, certain aspects will be briefly mentioned here. Cottonseeds contain an antioxidant which inhibits the oxidation of the oil contained in cottonseed meal after expression of the bulk of the oil. Miller (1935) has found that this natural antioxidant can be used to stabilize the vitamin A of cod liver oil in mixed feeds. By mixing this oil intimately with cottonseed meal before incorporating it in the feed, the loss of vitamin A during storage was markedly reduced. Soya beans, on the other hand, contain a substance which causes the rapid destruction of vitamin A in the presence of air. Frey and co-workers (1936) have studied this phenomenon and found that the substance responsible was rapidly destroyed by heating above 50°C. (which explains why it was possible to obtain a protective effect against oxidation of oils by the use of soya bean extracts, as described in Section 6 on rancidity. These extracts, it will be noted, were heated to 100°C. in the course of the experiment, so that the oxidant was destroyed while the antioxidant was, apparently, unaffected).

The changes in vitamin A potency during oxidation of a vitamin A concentrate were studied by Robinson (1938), using all three methods, biological, colori-

metric and spectrophotometric. The material, which consisted of the unsaponifiable fraction of a fish liver oil rich in vitamin A, was heated to 100°C. in the presence of oxygen and samples were taken at intervals.

TABLE X. Decrease in vitamin A potency of a concentrate during oxidation, as shown by three methods. Data are from Robinson 1938.

Time of heating (hours)	Biological activity (I.U. per g.)	$E_{1\ c.m.}^{1\%}$ 328mμ.	Blue value (B.U. per g.)
0	1,130,000	1070	56,000
3	770,000	810	34,000
9	290,000	450	14,000
24	50,000	270	5,000

The values found by each method decreased progressively (table X), but the relations between them were not constant. Robinson suggested that an oxidized form of vitamin A, which was biologically inactive but which showed absorption at 328mμ and gave a purple colour with antimony trichloride, was formed in the course of the destruction. It is obvious that this discrepancy, regardless of the actual reason for it, has an important bearing on the determination of vitamin A by either the physical or chemical method, since erroneously high values would be obtained with either in the case of oxidized material.

The nature of the solvent in which it is dissolved also has a marked effect on the stability of vitamin A. Dann (1932) studied the effect of various natural and artificial solvents on its destruction during aeration at 98°C. The percentages which were destroyed by aeration for one hour in the different solvents were as follows: butyl alcohol 0, amyl alcohol 22, cetyl alcohol 0, acetic acid 89, caproic acid 54, lauric acid 93, stearic acid 94, oleic acid 92, ethyl laurate 67, ethyl stearate 87, ethyl oleate 81, amyl acetate 23, triacetin 0, tributyrin 31, triolein 36, cocoanut oil 29, peanut oil 60, 20 per cent alcoholic potassium hydroxide 0, ethyl alcohol (at 78°C.) 0. The important part which the solvent plays in determining the rate of oxidation can be seen from these data. There is apparently no relationship between the rate of oxidation of vitamin A and the molecular constitution of the solvent, although it is worthy of note that the vitamin was destroyed more rapidly in all the acids studied, while the rate of destruction in some of the alcohols and esters, and in strong alcoholic potassium hydroxide, was negligible. The source of the vitamin A used in these experiments was a crude cod liver oil concentrate which showed approximately 100,000 blue units per gram by the antimony trichloride test. It was made up into solutions containing 1 per cent of the concentrate by weight.

Vitamin A is less susceptible to hydrogenation than might be expected from its highly unsaturated nature. Thus, while hydrogenation at high temperatures

is very destructive, an oil containing vitamin A may be hydrogenated at low temperatures without appreciable loss of potency. Drummond (1919) found that complete inactivation of vitamin A resulted when the oil was hydrogenated for four hours at 250°C. On the other hand, Waterman and his co-workers (1936) have shown that an oil may be hydrogenated at 50°C., a colloidal nickel catalyst being used, without an appreciable loss of vitamin A taking place.

Chlorination of cod liver oil was found by Diller (1938) to cause serious loss of vitamin A when more than 0.1 per cent chlorine was introduced, whether by hydrochloric acid, ammonium chloride or direct chlorination. The effect of a considerable number of reagents on the vitamin A in cod liver oil was investigated by Cady and Luck (1930). Bubbling sulphur dioxide through the oil for 15 minutes at 20°C. destroyed most of the vitamin A. Treatment with solid sodium bisulphate at 100°C. in a stoppered bottle caused no apparent loss in 4 hours, but in 24 hours destroyed the vitamin A. Bubbling hydrogen sulphide through at 100°C. for 6 hours caused significant, but not complete destruction, and a similar treatment with ethylene had no effect. Under the same conditions nitrous fumes, generated by the action of 20 per cent acetic acid on sodium nitrite, destroyed the vitamin. Neither ammonia gas bubbled through for 25 hours, nor dry formaldehyde for 1 hour, each at 100°C., had any effect on the vitamin, but chlorine gas destroyed it in 15 minutes at 100°C. When 50 cc. of the oil were shaken with 150 cc. of hydrogen peroxide for 5 minutes daily over a period of 18 days, partial destruction took place. Either 100 cc. of acetyl chloride or 50 g. of phosphorus pentachloride mixed with 100 cc. of the oil completely destroyed the vitamin A in 22 hours at room temperature.

Adsorption has played an important role in the numerous attempts which have been made to concentrate vitamin A. It can be adsorbed by soaps and by various finely divided inorganic substances. To be satisfactory for use in the concentration of vitamin A, an adsorbent must not only actively take up the vitamin under one set of conditions, but it must also readily give it up again under another set, without appreciable loss during the process. Not all substances which are active in adsorbing vitamin A fulfill the other requirements. Thus Holmes, Lava, Delfts and Cassidy (1933) found that while Norit, a vegetable carbon, was an excellent adsorbent for removing vitamin A from a solution of cod liver oil in petroleum spirits, recovery of the vitamin was very difficult. Holmes, Cassidy, Manly and Hartzler (1935) state that they have overcome the loss of vitamin A due to oxidation while adsorbed on carbon, but only by taking great precautions to remove air and replace it with nitrogen during the activation of the carbon. Silica gel will also adsorb vitamin A from cod liver oil. Toluene will remove the adsorbed vitamin from the silica gel but acetone will not.

Calcium oxide, calcium hydroxide, calcium carbonate, magnesium oxide, alumina and fuller's earth have all been used in the preparation of vitamin A concentrates by the Tswett method. In this method the adsorbent is packed evenly in a vertical tube and the crude vitamin A solution forced down through it by a gentle pressure or by suction, petroleum spirits being commonly used as the solvent. Since the different substances present in a crude solution of vitamin A differ in the extent to which they are adsorbed, they will gradually separate into bands when washed down the column with an excess of the solvent. Separation of the vitamin A rich fraction may be effected in either of two ways. In the first, after a period of washing with petroleum spirits to separate the bands, the column of adsorbent is forced from the tube, cut into a number of sections and each extracted with petroleum spirits containing 10 per cent methyl alcohol. This mixed solvent removes the vitamin. The fractions thus obtained are examined spectro-

photometrically or tested by the antimony trichloride test to determine their content of vitamin A. In the other method fresh quantities of the same solvent from which the vitamin is adsorbed are made use of, and the washing of the column continued until all of the vitamin A has been washed out. Frequent changes of receiver make possible the separation of a relatively pure vitamin fraction. An excellent description of the preparation and use of a Tswett column for the concentration of vitamin A is given by Castle, Gillam, Heilbron and Thompson (1934). Karrer and Schöpp (1932) have used this method to separate vitamin A, carotene and xanthophyll. They made use of a special adsorbing clay.

Adsorbents vary greatly in their ability to take up vitamin A. Not only do different adsorbing materials have markedly different capacities, but one substance will vary, depending on its source and the method of its preparation. Holmes, Lava, Delfts and Cassidy (1933), who investigated a number of different materials as adsorbents for vitamin A, found that an alumina prepared by slow crystallization from dilute sodium hydroxide solution, followed by heating to drive off most of the water of crystallization and washing to remove any sodium hydroxide remaining, was the most active of several tested. Further, it took up vitamin A from cod liver oil dissolved in petroleum spirits to a far greater extent than when dissolved in chloroform.

If an oil containing vitamin A, in which any appreciable amount of free fatty acids is present, is subjected to alkali refining with dilute alkali, some of the vitamin A will be found in the solution of soap which is formed. Brocklesby and Kuchel (1938) have shown that this is an adsorption phenomenon. Their strongest evidence for this was obtained from measurements of the relationship between the vitamin A potency of the original oil and the amount of vitamin A removed by the soaps. The results show the essentials of an adsorption isotherm. If the logarithms of the vitamin A concentrations of the original oils are plotted against the logarithms of the vitamin A removed, the points fall on a straight line. Further evidence was obtained from the effect of temperature on the process. It was found that, when 10 per cent of oleic acid was added to a halibut liver oil and then neutralized with dilute sodium hydroxide, the removal of vitamin A decreased as the temperature at which the neutralization was carried out increased. Sodium oleate tends to form true solutions at higher and colloidal solutions at lower temperatures, so that as the temperature is increased the capacity to adsorb decreases. If the phenomenon of the removal of vitamin A by soaps formed *in situ* actually is adsorption, it would naturally be implied that complete recovery of the vitamin removed from an oil by the soap should be possible. These authors found that none of the vitamin A thus removed was lost through oxidation during the adsorption process, and that it could all be recovered by adding barium chloride to the soap solution to destroy its colloidal properties and then extracting several times with chloroform.

The discovery of vitamin A was made through purely biological studies; its isolation was not accomplished until quite recently. The procedures which have been used for the preparation of highly purified concentrates are of particular interest here, since they illustrate possible methods of concentration on an industrial scale.

The first step in concentration is, generally, saponification of an oil rich in the vitamin and extraction of the unsaponifiable fraction, which contains vitamins A and D. Heilbron and his co-workers (1932) used two different methods for the purification of vitamin A. In the first method the unsaponifiable fraction of a potent halibut liver oil was dissolved in hot methyl alcohol and the sterols crystallized out by reducing the temperature to $-50°C$. The material remaining in solution was transferred to petroleum spirits, dehydrated and the solvent removed. The product was fractionated by distillation *in vacuo*. Most of it distilled at from 137 to 139°C., at a pressure below 0.0001 mm. The distillate was a pale yellow oil of very high vitamin A potency. In their other method fractional adsorption was used. The unsaponifiable matter of the fish liver oil was dissolved in petroleum spirits and the solution forced through a tube of specially prepared alumina. The middle section of the adsorbing column yielded, by extraction with hot methyl alcohol, a product substantially the same as that prepared by distillation.

The distilled product had the following chemical properties. It was readily soluble in organic solvents, somewhat more so in methyl than in ethyl alcohol. The purified vitamin was more resistant than crude solutions, such as fish liver oils, to oxidation by a stream of oxygen at elevated temperatures, but on standing, even in a sealed tube in the dark, a gradual decrease in potency occurred. Whereas crude vitamin A concentrates are strongly resistant to catalytic hydrogenation, the distilled products could be hydrogenated quite easily with either palladium or Adam's platinum oxide. The theoretical iodine value of vitamin A is 448 (five double bonds), the experimental values of three samples were respectively 306, 315 and 324, which indicates that the ethylene linkage of the ionone ring is resistant to halogenation. A benzoic acid ester of vitamin A was prepared by treatment with benzoyl chloride in pure dry pyridine.

Crystalline vitamin A has been prepared by Holmes and Corbet (1937). Their first step, like that of the above workers, was saponification of a fish liver oil rich in vitamin A, and extraction of the unsaponifiable fraction. This was dissolved in methanol. By careful adjustment of the concentration of the solution they were able to crystallize out most of the sterols by cooling to $-50°C$. After distilling off part of the solvent, and adding about 1 per cent of water, vitamin A slowly crystallized out at the same temperature. By recrystallization from methanol, crystals of relatively constant melting point were obtained. They appeared as radiating clusters of pale yellow needles, melting at from 7.5°C. to 8.0°C. and had an average molecular weight of 294. Biological assay of the crystalline products indicated that the potency was approximately 3,000,000 International units per gram.

(*b*) PROPERTIES OF VITAMIN D

(i) PHYSIOLOGICAL PROPERTIES

The function of vitamin D in the body is to regulate the assimilation of calcium and phosphorus. These two mineral elements, which, combined as tricalcium phosphate, give the hard structure to bones and teeth, must be supplied in the diet throughout the entire life of an individual, but in largest amounts during childhood. Improper calcium and phosphorus metabolism during childhood

results in rickets, a disease in which there is subnormal calcification of the growing bones. Normally the bones are calcified at the ends as they lengthen, but in a rachitic child, while they continue to grow, they are formed of cartilage incompletely calcified or, in extreme cases, not calcified at all. To compensate for the resulting weakness the ends of the long bones become greatly enlarged. This enlargement is a typical symptom of rickets. Another typical symptom is the "rachitic rosary". This is a line of knobs on each side of the chest, formed by enlargement of the junctions between the ribs and the cartilages. If rickets is allowed to continue for long, permanent deformities, such as bow legs, result. Besides man, all other mammals and birds appear to be susceptible to the disease.

Osteomalacia is the adult equivalent of rickets. In this condition more calcium and phosphorus is excreted than is ingested. A withdrawal of these minerals from the bones usually follows, resulting in structural breakdown, as evidenced by fragility.

While the skeletal changes described are the most prominent results of a rachitic diet, there are others also associated with such a dietary regime. Poorly formed teeth and increased susceptibility to rickets usually follow. In poultry an inadequate amount of vitamin D in the ration causes various pathological changes which will be dealt with in a later section.

The three main factors involved in the prevention of rickets, osteomalacia and associated disturbances are: (1) an adequate dietary intake of calcium and phosphorus salts, (2) a fairly close balance between the amounts of calcium and phosphorus in the diet, and (3) adequate vitamin D. When the relative amounts of calcium and phosphorus in the diet are well balanced the necessity for vitamin D is at a minimum. A great excess of either mineral, however, interferes with the absorption of the other. It is in such cases that vitamin D is needed most, since it enables the body to utilize most efficiently the calcium and phosphorus with which it is supplied. Addition of vitamin D to a diet in which there is a severely unbalanced calcium-phosphorus ratio brings about a resumption of more normal calcification.

Excessive doses of vitamin D are very toxic. They cause deposition of calcium salts in various organs and blood vessels. An amount of vitamin D equivalent to 100 times the minimum protective dose, which is one International unit per day, causes perceptible evidence of harmful action in the rat, 4,000 times is definitely injurious and 40,000 times strongly toxic. An overdosage of 100,000 times the protective dose is fatal.

There are several forms of vitamin D, differing from one another in the extent of their physiological activity. The fact that more than one individual compound can have vitamin D activity became apparent as a result of studies on the antirachitic effect of irradiated ergosterol. In 1924 Steenbock and Black showed that ultraviolet irradiation of diets which did not otherwise prevent rickets, gave them antirachitic properties. Cholesterol was first thought to be the substance which was thus activated. Subsequent work indicated that ergosterol, traces of which had accompanied the cholesterol previously studied, was the actual precursor of the antirachitic substance formed by irradiation. Massen-

gale and Nussmeier (1930) standardized a solution of irradiated ergosterol against cod liver oil with rats, and fed rat-equivalent quantities of each to chicks. They found that the cod liver oil vitamin D was approximately 100 times as effective as the irradiated material. This work has been amply confirmed by other investigators, and the vitamin D formed by irradiating ergosterol has been isolated and named calciferol. Cod liver oil and irradiated ergosterol, in amounts equipotent for rats, do not have the same antirachitic effect on children. The former is more effective, although irradiated ergosterol has, comparatively, somewhat more activity in man than in chickens.

It is now known that cholesterol itself can be activated. This can be done in several ways. Treatment with fuller's earth has a slight effect, but irradiation gives it a much stronger antirachitic potency. Heating purified cholesterol at temperatures slightly above its melting point for periods of from 1 to 3 hours considerably increases its activatability by ultraviolet irradiation. In equivalent rat dosages, irradiated cholesterol is more effective for chicks than irradiated ergosterol, but less so than cod liver oil.

There appear to be at least two, although possibly more, forms of vitamin D that occur naturally. Bills, Massengale and Imboden (1934) found that cod liver oil was approximately six times as potent with chickens as tuna liver oil, rat unit for rat unit. Bills (1937) reported comparative rat and chick vitamin D assays of tuna liver oil and the oil of the white sea bass, *Cynoscion nobilis*. The latter was twenty times as effective in chicks as the tuna liver oil.

(ii) CHEMICAL AND PHYSICAL PROPERTIES

The various forms of vitamin D all belong to the group of naturally-occurring organic compounds known as sterols. They are soluble, like vitamin A, in oils and oil solvents.

In many of the earlier studies on the chemical properties of vitamin D cod liver oil was used, and the effect of various treatments on its antirachitic activity measured. The vitamin D in this oil is considerably more stable to oxidation than vitamin A; it is, however, slowly destroyed when the oil is heated to 200°C., even in the absence of air. Neither saponification of the oil with boiling 20 per cent alcoholic potassium hydroxide, nor hydrogenation at 55°C. for 36 hours, using a colloidal platinum catalyst, has any effect on vitamin D. Free fatty acids in cod liver oil do not appear to have any destructive action on this vitamin. Sheehy (1932) found that the vitamin D potency of cod liver oil did not change during storage under ordinary conditions for 16 months. Payne (1930) stored cod liver oil mixed with ground grains for 12 months and found no loss of vitamin D. Bills (1925) studied the action of various reagents on this vitamin in a sample of Newfoundland cod liver oil. He observed that the vitamin was not affected by hydrogen peroxide, hydrogen sulphide, suphur dioxide or formaldehyde, but that it was rapidly destroyed by nitric oxide, and slowly by direct steam or contact with mineral acids.

Irradiation of certain sterols, as already pointed out, gives them antirachitic activity. The activation of ergosterol has been studied by many investigators, and as a consequence there is a

considerable amount of data available respecting the activation of that particular sterol. The products of its irradiation and the methods which have been used in separating them have been described by Eddy and Dalldorf (1937). These products have been given the following names, in the order of their formation: ergosterol, lumisterol, tachysterol, calciferol, substance 248 or toxisterol, and suprasterols I and II. Eddy and Dalldorf's description of these products is as follows:

"Lumisterol called Sterol 'x' by the English and Lumistearin by the Germans has the formula $C_{28}H_{43}OH$ and a melting point of 118°. It has apparently no antirachitic action. The Vitamin D1 of the German investigators was apparently Lumisterol plus calciferol (1/1).

"Tachysterol has the formula $C_{28}H_{43}OH$ and the melting point is as yet undetermined. It is removable from a crude irradiated ergosterol by citraconic anhydride and does not crystallize. It is probably devoid of antirachitic action and slightly toxic.

"Calciferol, true vitamin D, has the formula $C_{28}H_{43}OH$ and a melting point of 115-117°. It is not precipitated by digitonin. This property affords a means of separating it from cholesterol. One milligram of this substance represents 40,000 International units of vitamin D.

"Substance 248 or Toxisterol has not yet been satisfactorily isolated and chemically identified. It is apparently the substance that was responsible for the toxic action of the 'Vigantol' of the I. G. Farbenindustrie Aktiengesellschaft patent of 1928. It is not antirachitic. There is considerable evidence that it is more readily formed when ergosterol is irradiated in alcoholic solution.

"Suprasterols. Products of extreme irradiation were designated supra-stearine by Windaus, Gaede, Köser and Stein in 1930. They recognized two isomers, Suprasterol I and Suprasterol II. Suprasterols I and II have the common formula $C_{28}H_{43}OH$ but I melts at 104° and II at 110°. Neither has any antirachitic action and both are only slightly toxic."

It is thus evident that excessive irradiation destroys the vitamin D which was formed at an earlier stage in the process. The vitamin D in cod liver oil is likewise destroyed by ultraviolet irradiation. Wyman and co-workers (1927) showed that irradiation of cod liver oil with ultraviolet light for 20 minutes neither increased nor decreased the vitamin D potency, but irradiation for two hours markedly decreased it.

Several methods have been used in concentrating vitamin D from natural sources. Zucker (1922) concentrated the antirachitic factor of cod liver oil 1000 times. He extracted the oil with 95 per cent alcohol, saponified the extract and, by addition of a calcium salt, precipitated the calcium soaps. The vitamin D, which was adsorbed on the latter, was extracted from them with acetone. Acetic acid, formic acid and liquid ammonia have also been used to extract vitamin D from cod liver oil. Unlike other sterols, vitamin D is not precipitated by digitonin, so that this reagent can be used to separate it from biologically inactive sterols.

Brockmann (1936) isolated vitamin D from tuna livers by the following procedure. The unsaponifiable fraction of tuna liver oil was dissolved in benzine, and the solution extracted with 90 per cent methyl alcohol. The bulk of the vitamin A was taken up by the methyl alcohol and thus eliminated. The vitamin D was then extracted from the benzine solution with 95 per cent methyl alcohol. Further purification was accomplished by fractional adsorption on a column of alumina. The cholesterol was then removed and the vitamin D esterified with 3, 5-dinitrobenzoyl chloride. The ester was adsorbed on alumina from benzine, and eluted with methyl acetate. Addition of methyl alcohol gave a crystalline 3, 5-dinitrobenzoate of vitamin D which melted at 128° to 129°C.

Saponification with 5 per cent potassium hydroxide in methyl alcohol liberated the vitamin as an oil, the potency of which was 25,000 International units per mg.

Simons and Zucker (1936) obtained a product essentially the same as Brockmann's but by a somewhat different procedure. Their starting material was also an alcohol-soluble fraction of the unsaponifiable matter of tuna liver oil. The sterols were esterified with phthalic acid in order to separate them from the hydrocarbons. The sterol mixture was fractionated by distribution between solvents and the cholesterol removed with digitonin. Freezing, decolorization with carbon, and finally formation of the 3, 5-dinitrobenzoic acid ester gave a crystalline product melting at 128.5°C. Its vitamin D potency was 30,000 International units per mg.

Short-path distillation was used by Hickman and Gray (1938) in the examination of natural vitamin D from several sources. Distillation of a preparation of vitamin D from Norwegian cod liver oil yielded two main active fractions, indicating the presence of two chief vitamins. There were two others present in smaller quantities and traces of two more. The curves obtained in the distillation of the vitamin D from the liver oils of the white sea bass and the Japanese spearfish indicated that each contained a form of the vitamin different from the other. Distillation of vitamin D from the liver oil of the long-finned tuna gave some indication that a single form preponderated in it, but the vitamin D in this oil was so unstable to heat that no definite conclusion could be drawn from this experiment.

While the presence of several forms of vitamin D in natural oils has thus been indicated by short-path distillation, only one form, vitamin D_3, has been definitely isolated from natural sources. Vitamin D_3, which is the irradiation product of 7-dehydrocholesterol, has been isolated from tuna and halibut liver oils. Evidence that other apparently pure substances which have been prepared differ from this, is somewhat inconclusive.

(c) CANADIAN SOURCES OF THE VITAMINS

(i) RELATIVE IMPORTANCE OF CANADIAN SOURCES

Oils containing vitamins A and D are produced on both the Atlantic and Pacific coasts of Canada. Whole fish unsuitable for food purposes, fish livers, viscera and cannery waste constitute the raw materials from which these oils are made. In table XI statistical data are given showing the production of such oils and the landings of the raw materials in the various provinces of Canada for the years 1936 to 1938.

While the data are, for the most part, self-explanatory, there are several features that require elaboration. "Medicinal" cod liver oil is the best grade of cod liver oil, prepared by steaming fresh cod livers and skimming off the separated oil. "Cod oil" includes oil prepared from stale livers, as well as that obtained by further steaming and pressing of the residues from the preparation of medicinal oil. Cod oil is not as suitable as the latter oil for medicinal purposes, but is used to a considerable extent for poultry. Some is also used for industrial purposes.

At present cod liver oil, cod oil and swordfish liver oil and horse-mackerel liver oil are produced only on the Atlantic coast, pilchard and salmon oils, black ling- and red-cod liver oils only on the Pacific. Herring and grayfish oils, as well as halibut livers are produced on both coasts but the production on the Pacific coast is in each case considerably larger than that on the Atlantic. The total

TABLE XI. Canadian production

		Prince Edward Island			Nova Scotia			
		1936	1937	1938	1936	1937	1938	1939
Cod, medicinal oil	gal.			1,989	50,031	42,036	46,352	
Oil	gal.	1,580	5,046	2,888	53,576	82,340	76,153	
Hake oil	gal.				100			
Pollock oil	gal.				2,000	850	400	
Halibut livers	cwt.				844	570	676	
Liver oil	gal.							
Viscera oil	gal							
Herring oil	gal.						7,020	
Pilchard oil	gal.							
Salmon oil	gal.							
Black cod livers	cwt.							
Liver oil	gal.							
Ling cod livers	cwt.							
Liver oil	gal.							
Red and rock cod livers	cwt.							
Liver oil	gal.							
Red cod viscera	cwt.							
Tuna livers	cwt.					23	25	
Grayfish livers	cwt.							
Oil	gal.				11,925	9,810	19,650	
Swordfish livers	cwt.					138	39	370
Shark livers	cwt.							

amount of oil produced on the Pacific coast of Canada is also considerably in excess of the total Canadian Atlantic coast production.

In table XII the vitamin potencies of some marine animal oils produced or imported into Canada are listed. It must be emphasized that the ranges of vitamin potencies given are not to be taken as rigid. Great variations in vitamin

of vitamin-containing fish oils.

New Brunswick			Quebec			British Columbia			
1936	1937	1938	1936	1937	1938	1936	1937	1938	1939
3,100		391	17,327	7,490	13,882				
2,650	12,021	1,605	32,005	23,415	28,474				
6,036	1,750	2,937							
6,462	2,275	690							
			12	10		1,916	1,782	3,049	3,853
							843	750	650
								815	688
27,751	29,679	92,198				782,499	1,283,658	929,158	1,383,341
						1,217,097	1,707,276	2,195,850	199,957
						171,326	169,239	114,797	128,170
						235	298	397	382
								50	106
						1,195	518	830	793
								31	145
							11	26	16
								88	80
									2
									50
								9,333	602
						164,643	124,464	113,360	130,034*
267									
.									6

*Includes: 17,501 gal. liver oil.

TABLE XII. Vitamin potencies of some marine animal oils.

Family	Common name	Source of oil	Oil %	Vitamin A (B.U./g.)		Vitamin D (I.U./g.)	
A. Produced on the Pacific coast							
ELASMOBRANCHII							
Cetorhinidae.....Basking-shark		liver	?–80	0–	500	......	
Galeidae.........Mud shark and soup-fin shark		liver	40–70	1,000–	150,000	5–	25
Squalidae........Grayfish or dogfish		liver	40–70	500–	20,000	5–	25
		viscera	2– 4	2,000–	4,000	......	
		body	3– 5	25–	400	......	
Rajidae..........Rays or skates		liver	40–70	100–	1,000	5–	25
HOLOCEPHALI							
Chimaeridae......Ratfish		liver	40–70	100–	500	0–	5
TELEOSTOMI							
ISOSPONDYLI							
Clupeidae........Pilchard		liver	6– 8	20,000–	40,000	200–	300
		body	8–25	50–	100	20–	80
	Herring	liver	3– 5	20,000–	40,000	200–	300
		body	8–15	50–	100	20–	80
Salmonidae.......Salmon							
	Steelhead	liver	10–20	10,000–	20,000	100–	500
		viscera	20–40	1,000–	2,000	......	
	Sockeye	liver	4– 6	10,000–	40,000	200–	600
		viscera	4– 8	10,000–	20,000	......	
	Chum	liver	4– 6	5,000–	10,000	100–	500
		viscera	2– 4	500–	1,000	......	
	Spring	liver	4– 6	10,000–	40,000	100–	500
		viscera	2– 4	1,000–	5,000	100–	200
	Pink	liver	4– 6	5,000–	10,000	100–	500
		viscera	2– 4	5,000–	10,000	......	
	Coho	liver	4– 6	10,000–	20,000	100–	500
	Salmon offal		4– 8	100–	500	100–	300
	Salmon egg			10–	100	5–	25
LORICATI							
Anoplopomatidae .Black cod		liver	10–30	15,000–	60,000	600–	1,000
		viscera	4–10	10,000–	80,000	100–	200
Ophiodontidae....Ling cod		liver	6–10	50,000–	500,000	1,000–	6,000
		viscera	8–16	25,000–	150,000	100–	200
Scorpaenidae.....Red cod		liver	5–15	90,000–	500,000	1,000–	5,000
		viscera	4–10	10,000–	80,000	100–	200

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TABLE XII—*Continued*

Family	Common name	Source of oil	Oil %	Vitamin A (B.U./g.)	Vitamin D (I.U./g.)
ANACANTHINI					
Gadidae.........Gray cod		liver	20–40	1,000– 20,000	100– 500
		viscera	1– 5	8,000– 40,000	10– 35
HETEROSOMATA					
Pleuronectidae....Halibut, round-nosed					
	sole, etc.	liver	10–30	8,000–200,000	1,000– 5,000
		viscera	1– 5	20,000–400,000	100– 500
		head	10–20	60– 100	5– 10
	Flounders and soles	liver	8–10	10,000– 30,000	1,000– 2,000

MAMMALIA

Family	Common name	Source of oil	Oil %	Vitamin A (B.U./g.)	Vitamin D (I.U./g.)
CETACEA					
Balaenopteridae ..Whale		liver	4– 6	90,000–200,000	0– 5
		blubber	80–90	<100	......
Delphinidae......Porpoise		liver	4– 6	20,000– 30,000	......
		blubber	80–90	20– 30	......
PINNIPEDIA					
Otariidae.........Hair seals		liver	2– 4	8.000– 10.000	......
		blubber	80–90	40– 50	20– 40
	Sea lions	liver	2– 4	10,000– 20,000	200– 300
		blubber	80–90	200– 400	20– 40

B. Produced on the Atlantic coast

TELEOSTOMI

Family	Common name	Source of oil	Oil %	Vitamin A (B.U./g.)	Vitamin D (I.U./g.)
ANACANTHINI					
Gadidae.........Cod		liver		1,000– 6,000	50– 150
	Haddock	liver		100– 300	50– 75
	Pollock	liver		2,000	110
Merluciidae......Hake		liver		1,600	10– 130
PERCOMORPHI					
Xiphiidae........Swordfish		liver	15–20	10,000–400,000	2,000–14,000
Scombridae......Horse mackerel or blue-					
	fin tuna	liver		55,000	16,000
Anarhichadidae...Wolf fish		liver		1,000	20

C. Imported into Canada

Distribution

TELEOSTOMI

Family	Common name	Source of oil	Oil %	Vitamin A (B.U./g.)	Vitamin D (I.U./g.)
PERCOMORPHI					
Scombridae...	.Blue-fin tuna or horse mackerel, albacore, bonito, Pacific mackerel, yellow-fin tuna, striped tuna or skip-jack.	World-wide distribution and tendency to southern warm waters, i.e. Columbia river — Southern California.		20,000–500,000	5,000–60,000

TABLE XII—*Continued*

Family	Common name	Distribution	Vitamin A (B.U./g.)	Vitamin D (I.U./g.)
Carangidae.......	California yellowtail	California coast	50,000	17,000
Sphyraenidae.....	California barracuda	California coast	40,000	2,000
Sciaenidae.......	Totuava (croaker)	Warm seas, Atlantic & Pacific	50,000–100,000	. . . . . .
Gempylidae......	Australian barracuda	Southern Pacific	30,000– 70,000	up to 300
Serranidae.......	Black sea bass or jewfish, rock bass, cabrilla, ishinagi, etc.	Warm seas, Atlantic & Pacific.	15,000–500,000	1,000– 4,000
LORICATI				
Scorpaenidae.....	Boccacio, Chile-pepper	Pacific Ocean, temp. waters.	50,000–500,000	300– 5,000

potencies occur in these oils, and while the above table was constructed from as many data as were available, further work on more samples may show that these ranges may have to be modified. In spite of this, the data in the table serve to emphasize several important facts. The liver oils of the Percomorphi are outstanding in their high vitamin D potencies, the only other oils approaching them being those of the Loricati and, to a more limited extent, the Heterosomata. On the Atlantic coast of Canada the livers of two fish belonging to the Percomorphi are now being utilized for their oil content; these are the swordfish and the horse mackerel (tunny or tuna). The true mackerel of the Atlantic coast, which constitutes an important fishery, also belongs to the Percomorphi, but no published data regarding the vitamin potency of the liver oil are available and apparently the livers are not processed for their oil content. On the Canadian Pacific coast the only fish of the Percomorphi caught commercially is the albacore and this fishery is still in its infancy, the first commercial catches being taken during 1939. Thus the domestic supply of liver oils of high vitamin D potency is somewhat limited and this accounts for the importation of considerable quantities of livers of the Percomorphi from California and Japan. The orders Isospondyli and Anacanthini include fish, the oils of which are important sources of vitamin D. Although the actual potencies of these oils are much lower than those of the three orders mentioned above, the total amount of oil available is much greater. Thus cod liver oils and the various oils of the salmon, pilchard and herring are capable of supplying a large amount of vitamin D but in less concentrated form than that found in the oils of the Percomorphi. Finally, oils of the fish groups Elasmobranchii and Holocephali contain very little vitamin D, as also do the blubber and liver oils of the mammalian group, Cetacea.

Vitamin A is more widely and generously distributed. Although its potency does not always parallel that of vitamin D, it is to be observed that the three orders, whose members show the highest vitamin D potency, are also the highest

in vitamin A. However, practically all fish liver and visceral oils contain considerable amounts of this vitamin. The potencies vary through very wide ranges, particularly in fish of the groups Elasmobranchii and Holocephali. It is questionable whether the oils from the livers of the marine mammals are as rich in vitamin A as they would seem to be from the blue values quoted in the table. Haines and Drummond (1938) have shown that whale liver oil contains a substance which is not vitamin A, but which has an intense selective absorption in the same region of the spectrum as that vitamin. Oils containing vitamin A are available from fish caught on both the Atlantic and Pacific coasts of Canada and it would seem that the supply is adequate for domestic requirements. The vitamin A market is highly competitive, however, and at times it is more economic
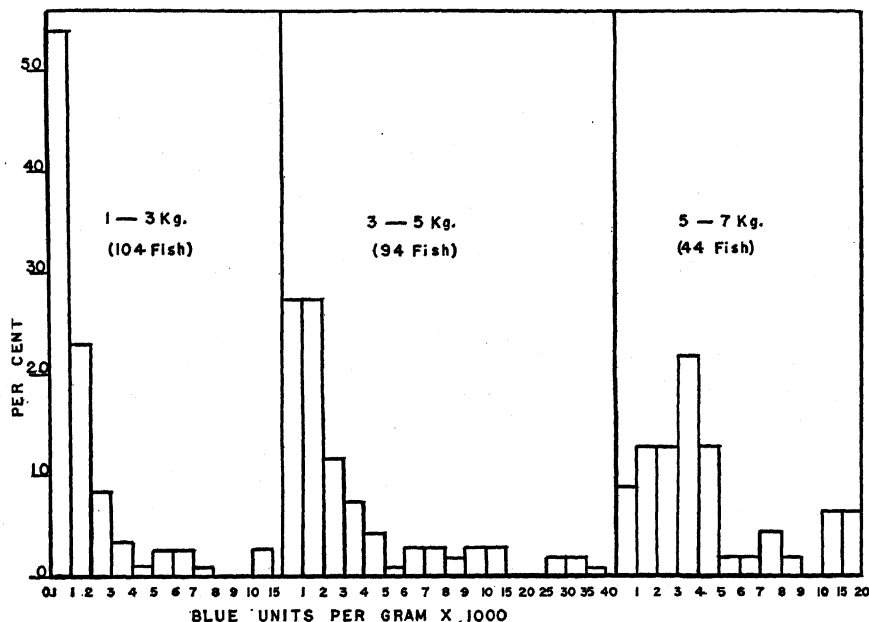
FIGURE 5. The relation between the weight of the grayfish and the vitamin A content (blue value) of the liver oil. The lower potency groups increase by 1,000 units and the higher potency groups by 5,000 units.

to import fish liver oils of high vitamin A potency than to produce the oils domestically. This situation exists in connection with certain shark liver oils, notably soup-fin-shark liver oil, produced in California. This oil is very high in vitamin A and the cost of production is relatively low. The oil is thus a very cheap source of the vitamin and is imported into Canada at the present time.

(ii) FACTORS INFLUENCING VITAMIN POTENCY OF CANADIAN FISH OILS

It is very important that producers of fish oils which are to be used as sources of vitamins should have as much information as possible concerning the factors which influence the vitamin potency of the oils which they are producing. It is

particularly so when part of the season's production is used as a source of vitamins, and part for industrial purposes. In such cases, if the producer knows under what conditions the oil may be expected to have the highest vitamin potency, he is in a better position to select the part of his production to be used nutritionally.

Pugsley (1939a) has studied the factors influencing the vitamin A and D potency of grayfish liver oil. He concluded that the vitamin A potency was related mainly to the size, and thus the age, of the fish, the larger or older fish yielding liver oils of higher vitamin A blue value than the smaller or younger fish. The relationship between the weight of the fish and the vitamin A blue value of the liver oil is shown in figure 5.

The vitamin A potency was also related to some extent to the colour of the oil. Most of the oils containing 10,000 or more blue units per gram were from livers brown in colour and presenting a mottled pattern, rather than from the light yellow or cream-coloured livers which in general yielded paler oils, of lower potency. The colour of the oil, blue value and E value of pooled monthly samples of grayfish liver oil from fish taken in 1936-1937 are given in table XIIIA. These data do not show any seasonal trend.

The vitamin D potencies of three samples of grayfish liver oil were determined by bio-assay. The data obtained, together with the vitamin A potencies

TABLE XIII

A. Colour of oil, blue value and E value of pooled monthly samples of grayfish liver oil.

Month (1936-7)	Amt. of oil (kg.)	Colour (yellow)	Blue units per g.	$E_1^{1\%} c.m.$
November........	8.72	2.4	1100	1.18
December........	2.32	2.0	500	0.64
February.........	4.06	5.6	5000	6.45
March...........	6.54	3.4	1750	1.70
May.............	6.54	3.6	2300	2.42
July.............	4.41	4.2	2900	3.20
August...........	4.09	5.0	4000	4.48
September........	6.00	2.8	1250	1.23
October..........	3.43	3.4	3500	4.12

B. Vitamin D potency of grayfish liver oil.

No.	Av. wt. of fish kg.	Vitamin A Blue units per g.	Vitamin D International units
1	1.20	420	6
2	2.60	3200	7
3	4.40	28100	4

of these samples, and the average weight of the fish from which they were obtained, are given in table XIIIB. It is evident that there is no relation between vitamin D potency and either of the other factors presented in this table.
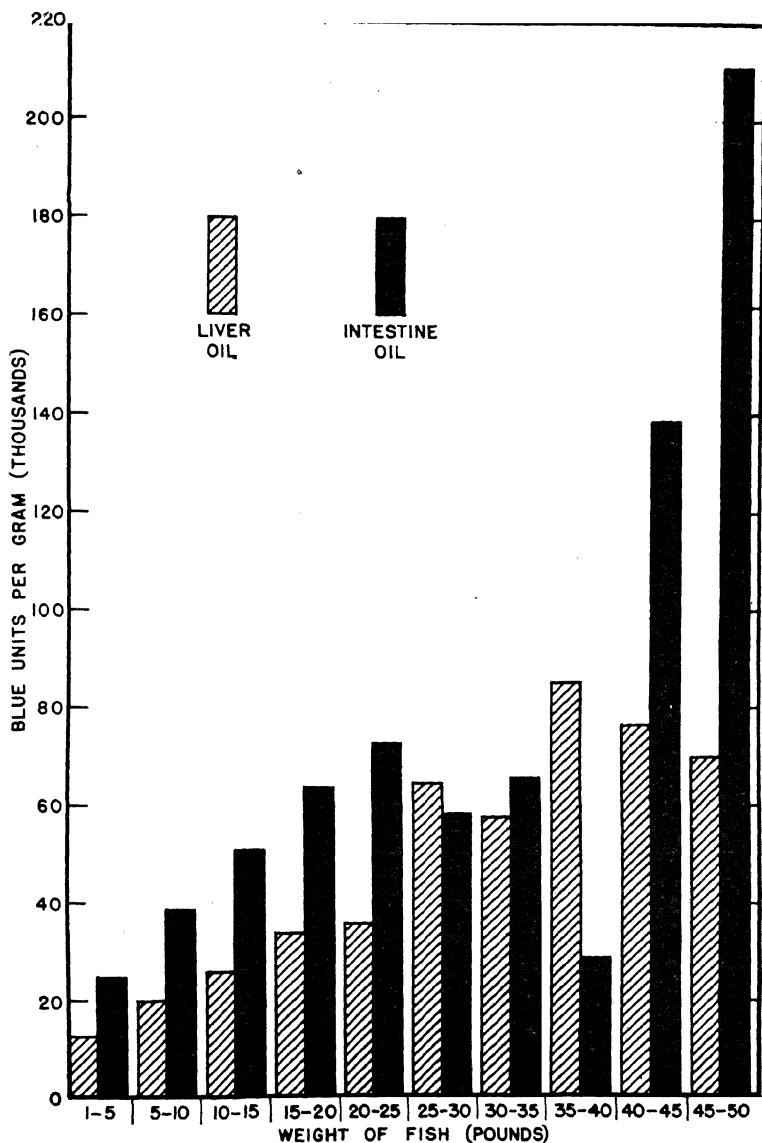

FIGURE 6. Vitamin A content (blue value) of halibut liver and intestinal oils in relation to increasing weight (age) of fish.

The same author (1939b) has studied the factors influencing the amount and vitamin A and D potency of the liver and visceral oils of the Pacific halibut. As with grayfish, the size of the fish appeared to be the most important factor in determining the vitamin A potency of the liver oil, and in this case, of the visceral oil also. The oil content of neither the liver nor the viscera showed any relation to the weight of the fish. The yields and vitamin A contents of these oils in relation to the weights of the halibut are shown in figure 6.

While the percentage of oil in the viscera did not alter significantly from month to month, the oil content of the livers tended, in general, to be higher during the summer months than during the spring and fall. There was an inverse relationship between the amount of oil in the liver and the vitamin A content of the liver oil. Thus the vitamin A potency of the liver oil tended to be lower during the summer than during the preceding or following months.

The vitamin D potencies of a number of samples of liver oils were determined. The values found showed considerable variation, but were, in general, higher for samples obtained from fish caught during the summer months than for those obtained from fish caught during the early spring and fall. The vitamin D potency of the liver oil did not appear to be related to the size of the fish, nor to the vitamin A content of the oil.

Pugsley (1939c) has also investigated the seasonal variations in vitamin A and D potency of the liver and intestinal oils of the Pacific gray cod. He found that during the fall and winter months there was a greater percentage of oil in the livers but a decreased potency of the oil in vitamins A and D than at other times.

Seasonal variation is also the predominant factor affecting the vitamin A and D potency of pilchard oil, the oil prepared from whole pilchards. In table XIV the oil yields and vitamin A and D potencies of a number of samples of pilchard oil produced in British Columbia in 1937 and 1938 are given. These data are taken from the report of Pugsley (1939d).

TABLE XIV. Seasonal variations in the vitamin potencies of pilchard oil.

Date of production	Stated yield (U.S. gal. per ton of fish)	Vitamin D (International units per g.)	Vitamin A (blue units per g.)
Aug. 1- 4, 1937	30	95	150
Aug. 16-18, "	51	50	240
Sept. 1- 3, "	56	35	60
Oct. 3- 5, "	50	70	220
July 29-31, 1938	40	100	125
Aug. 27-29, "	51	65	250
Sept. 15-18, "	55	55	260
Oct. 1- 3, "	60	50	230

It has been found in these laboratories by the writer that the blue value is not a satisfactory method of measuring the vitamin A potency of pilchard oil; therefore, too much credence must not be placed on the blue values given in the table. The increase in yield of oil as the season progresses, and the corresponding decrease in vitamin D potency of the oil is shown particularly by the figures for 1938. The progressive increase in yield of oil is a well established feature of this industry. The decrease in vitamin D potency which accompanies the increase in oil yield, and as well the seasonal trend, confirm the data previously obtained in these laboratories by Bailey (1935).

The pilchard fishery of British Columbia is an offshore fishery, and probably the fish all belong to the same general population. Pilchards delivered by the fishing boats to plants located at different points have usually all been caught in one locality. Since all the fish move up the coast in a general northerly direction as the season progresses, the locality of catching is to a great extent a function of the time in the season when the fish are caught. Local variation is thus automatically ruled out as a separate factor affecting the vitamin potency of the oil.

The herring fishery, on the other hand, is largely an inshore fishery. There are many local populations of herring which differ from one another with respect to such factors as their age-weight relationship, vertebral count, etc. It might thus be expected that locality of catching would be an important factor in connection with the vitamin potency of herring oil.

Very few data respecting the vitamin potency of Canadian herring oil are available. Those in table XV, which are taken from the report by Pugsley (1938), give no information regarding the possible factors related to the variations in potency. They show no regularity of variation with season or locality of catching, or with colour.

TABLE XV. The vitamin A and D potency and colour of British Columbia herring oils

Date of production	Locality of catching	Colour (Lovibond units)		Vitamin A, (blue units per g.)	Vitamin D, (International units per g.)
		yellow	red		
Oct. 15, 1936	Barclay sound............	10.2	0.6	25	30
Oct. 15, "	Esperanza inlet..........	21.0	1.7	20	50
Oct. 15, "	Cousins inlet............	21.0	1.0	76	50
Nov. 15, "	Esperanza inlet..........	25.0	1.3	26	65
Nov. 27, "	Cousins inlet............	12.0	0.4	30	75
Dec. 14, "	Esperanza inlet..........	25.0	1.5	28	35
Jan. 23, 1937	Barclay sound...........	27.0	0.7	30	50
Mar. 8, "	Prince Rupert harbour....	30.0	0.7	38	50
Mar. 8, "	Prince Rupert harbour....	29.0	1.4	19	75
Mar. 17, "	" " (body oil) ..	20.0	1.0	6	30
Mar. 17, "	" " (liver oil)...	very dark		22,500	250

The same criticism should probably be made of the use of the blue colour test for vitamin A in herring oil as was made respecting its use with pilchard oil.

Oils such as British Columbia pilchard and herring oils, which are prepared from the whole fish, may derive an appreciable part of their vitamin A potency from the contents of the stomach. The same may be the case with visceral oils when the stomach is included with the material processed. The nature of the food of the fish may thus be a significant factor affecting the vitamin A potency of the oil. Drummond and Gunther (1934) have investigated the vitamin A and D potencies of the oils from phytoplankton (green feed) and zooplankton (red feed). They found that the phytoplankton oil was considerably more potent than the zooplankton oil in its growth-promoting action. This was correlated with a greater richness of the former in carotene, which, as pointed out in an earlier part of this Bulletin, is converted to vitamin A in the animal body. Vitamin D was not present in significant amounts in either the phytoplankton or the zooplankton.

Only a very limited amount of data is available regarding the variations in vitamin potency of cod liver oils produced on the Atlantic coast of Canada. Macpherson and Wilson (1934) have, however, investigated the relationship between the age of Newfoundland cod and the vitamin A potency of the liver oil. In most cases the vitamin A potency was a direct function of the age (and size) of the fish, although there were exceptions. It is worthy of note that, while only three samples of the oil contained less than 1,000, and only three over 5,000 International units of vitamin A per gram, the former were all from fish less than 60 cm., and the latter all from fish more than 130 cm. in length.

II. PIGMENTS

Fish oils vary greatly in colour. Some, such as cod liver oil, may be almost colourless, while others, such as salmon oil, are dark red or brown. In many of the industries using fish oils, only light coloured oils are acceptable, so that a consideration of the factors governing the colour is very important to the producer. The two general causes of the colouration of fish oils are, (1) the natural oil-soluble pigments which occur in the fish, and (2) chemical changes in the oil which take place subsequent to the time the fish leaves the water, producing artificial pigments which also give it colour.

(a) NATURAL PIGMENTS

Most of the red, orange and yellow oil-soluble pigments occurring in plant and animal tissues belong to the class known as the carotenoids, the name being derived from carotene, the principal pigment of carrot roots, which was the first of this group to be isolated. The researches of Euler, Euler and Hellström (1928), Moore (1929) and others have shown that several of the carotenoid pigments have vitamin A activity. These "vitamin A precursor" pigments are formed in

plants, and converted to the vitamin itself, which is colourless, in animal organisms. Not all carotenoids have this physiological property. Most of them are without vitamin A activity.

The pigments which have vitamin A activity have not been found in significant quantities in commercial fish oils. Pilchard oil contains a little carotene, the commonest precursor of vitamin A. The Swedish workers Euler, Hellström and Malmberg (1933) reported finding a small amount of carotene in salmon oil, but it has not been found in various Pacific salmon oils which have been examined in these laboratories.

A fish oil does not, however, have to contain a large amount of the active pigments to be rich in vitamin A, since fishes, like other forms of animal life, are able to convert the active pigments which they get in their food into vitamin A. It is interesting to note, however, that the potency of individual fish liver oils in the colourless, preformed vitamin A is frequently in proportion to their degree of pigmentation. This is apparently due to a parallelism between the storage of vitamin A and the inactive carotenoid pigments in the livers of the fish.

Of the non-active pigments, astacin, first discovered in the shell of the lobster, appears to be the most common in marine oils. Its presence in red whale oil was indicated by Schmidt-Nielsen, Sörensen and Trumpy (1932) and Burkhardt and co-workers (1934). Sörensen (1935) isolated it from salmon oil. Bailey (1937) has found that the red colour of sockeye salmon oil is due to the presence of two astacin-like pigments. Astacin has also been found in the livers, roes and flesh of various other fish.

Biely and Chalmers (1936) indicated that the principal yellow pigment of pilchard oil was fucoxanthin, an inactive pigment which originates in various marine plants and reaches the pilchard either directly, when it is feeding on microscopic plant life of the sea, or is transferred to them by microscopic animal life when the latter constitutes their food.

The pigments of several samples of pilchard oil have been studied in these laboratories. Fucoxanthin was found in varying amounts in all the commercial oils, but was completely absent from two samples of oil prepared from the muscle only. It is thus apparent that the fucoxanthin in commercial pilchard oil must be derived from the viscera or the feed in the viscera. Pilchard oil also contains some xanthophyll, another pigment which does not act as a precursor of vitamin A in animal nutrition.

When pilchards are feeding on the so-called "green feed", which consists of microscopic green plant material, the oil produced has a greenish colour. This tint is stated by Tompkins (1930) to be due to the presence of chlorophyll, the green colouring matter of plants, which is dissolved in the oil from the feed in the intestines of the fish.

(b) PROPERTIES OF PIGMENTS FOUND IN FISH OILS

Three isomeric forms of carotene have been found in nature, but, since the properties which are to be considered here are largely the same for all three, they

will be referred to collectively as carotene. Carotene is a hydrocarbon. Its solution in oil as well as in most organic solvents is yellow to golden yellow, depending on the concentration, while the carbon disulphide solution is orange red to blood red. Carotene solutions are not affected by alkalies, but the pigment is quite susceptible to oxidation, being rapidly destroyed when an oil containing it is heated in the presence of air, and more slowly destroyed when the oil is exposed to the air at room temperature. Carotene in solution is also slowly destroyed when the solution is exposed to light.

Just as there are several isomeric carotenes, several xanthophylls have been recognized, but since the properties of these various xanthophylls also are quite similar to one another they will be referred to in this discussion simply as xanthophyll. This group of pigments give yellow solutions in oils and in many organic solvents. Their solutions in carbon disulphide are, however, orange red, never blood red. Saponification of a xanthophyll solution with 20 per cent alcoholic potassium hydroxide apparently does not affect the pigment, which can be separated in the unsaponifiable fraction along with the other carotenoids which are not affected by saponification. Xanthophyll can be separated from carotene by shaking a solution of these two in petroleum spirits with 90 per cent methyl alcohol. The xanthophyll is taken up by the alcohol while the carotene remains in the petroleum spirits. While xanthophyll is destroyed by oxidation it is, in general, not so labile as carotene.

Fucoxanthin can be extracted from a mixture of carotenoid pigments dissolved in equal parts of ethyl ether and petroleum spirits with 70 per cent methyl alcohol. Some xanthophyll is also extracted along with the fucoxanthin but it can be separated from the latter by shaking the 70 per cent methyl alcohol extract with a mixture of 5 parts of petroleum spirits and 1 of ethyl ether, which takes up the xanthophyll but not the fucoxanthin. When an ethereal solution of fucoxanthin is shaken with 30 per cent hydrochloric acid the ether layer is bleached, and a deep blue colour is formed in the acid layer. Some other pigments will, under these conditions, impart a green colour to the acid layer, but fucoxanthin can be distinguished by the deep blue colour which it causes.

Pure fucoxanthin is insoluble in petroleum spirits, but the presence of a small amount of fatty material makes possible its solution in that solvent. The ether solution of fucoxanthin is orange yellow, the alcoholic solutions have a brownish yellow tinge and the carbon disulphide solution is deep red. It gives a yellow colour to oils in which it is dissolved. Fucoxanthin solutions are less stable to light than those of most other carotenoids, bleaching out quite easily. This pigment has apparently no acid properties but under certain conditions is attacked by alkali. It can be dissolved in very concentrated aqueous solutions of potassium hydroxide, and cannot be extracted from such solutions by ether. Heating an oil containing fucoxanthin to 115°C. in the absence of air does not destroy the pigment.

Astacin occurs in fish oils in the form of esters which, like the oil itself, can be saponified by the action of strong alkalies. Apparently this pigment can act

chemically as an alcohol or as an organic acid, since, when the astacin ester is saponified, an alkali metal compound of astacin is formed. The latter is quite similar in its behaviour to the fatty acid soaps and cannot be extracted from the alkali solution with the unsaponifiable fraction. The free pigment can be liberated along with the fatty acids by acidifying the saponified material. Under certain conditions the alkali metal compound of astacin separates out at the alkali-ether interface when the unsaponifiable fraction is being extracted from the soaps with ether. When this occurs the precipitated astacin compound can be isolated from the rest of the material for examination. According to Lederer (1935) the free pigment, which can be liberated by acidification with acetic acid, is insoluble in water, very slightly soluble in ethyl ether, petroleum spirits and methyl alcohol, somewhat more soluble in benzene and ethyl acetate, and very soluble in chloroform, carbon disulphide, dioxane and pyridine. Like other carotenoids its solubility is strongly affected by the presence of fatty material. Astacin bleaches slowly when an oil containing it is exposed to light, and is rapidly destroyed when it is heated in the presence of air.
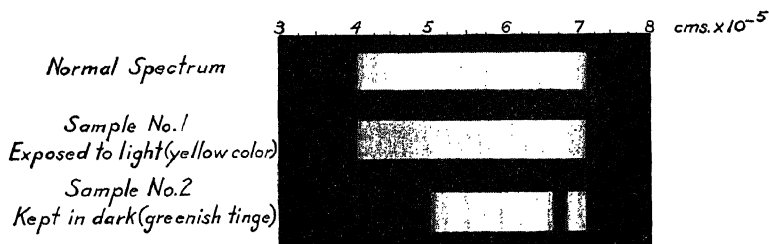
FIGURE 7. Absorption spectra of pilchard oil.

When an ether solution of chlorophyll is treated with a strong alkali, it first turns brown and then back to the original green, owing to the formation of a stable alkali salt which has a green colour. This alkali salt is soluble in water but insoluble in ether, as can be shown by diluting its alkaline solution with water and shaking with ether. No amount of dilution will cause the colour to go into the ether layer.

The greenish colour of an oil containing chlorophyll is stable in diffused light but disappears when exposed to direct light. Figure 7 shows the absorption spectra of two samples of an originally green-tinted oil. Sample 1 was exposed to the sunlight for a day and sample 2 was kept in the dark. It will be noticed that in addition to absorbing the blue part of the spectrum more sharply the sample kept in the dark has a well-defined absorption band in the red (6.55 to 6.75×10^{-5} cm.). This band disappears when the oil is exposed to sunlight but may be reproduced after a further period in the dark. The presence of this absorption band adds support to the idea that the green colour is due to the presence of chlorophyll, since that pigment has a very strong absorption band at 6.29 to 6.55×10^{-5} cm.

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(c) Colour Development During Preparation and Storage of an Oil

The chief factors which govern the darkening of fish oils and fish liver oils during preparation and storage are: (1) putrefaction of the fish between the times of catching and processing; (2) the temperature to which the oil is heated and the length of time that it is kept at an elevated temperature; (3) rancidification. The presence of small amounts of various foreign materials in a fish oil will also lead to darkening.

For the production of light coloured oils it is essential that the raw materials should be as fresh as possible when they are processed. Oils produced from stale material are darker than those made from fresh. Drummond and Hilditch (1930) studied the effect of the time of storage of cod livers on the quality of the resulting oil, and obtained the following results:

Age of livers (days)	1	2	3
Colour of oil (Lovibond units)—Yellow	3.3	3.8	4.6
Red	0.1	0.1	0.2

The same principle applies to whole fish or fish waste as to fish livers.

Partial decomposition of the raw material before processing also leads to other causes of subsequent darkening of the oil. Protein decomposition products dissolve in the oil and cause it to form stable emulsions which can be broken only by long heating. This, as already pointed out, leads to darkening of the oil. Even after breaking, the oil from such emulsions contains an unusually high content of water, suspended as droplets. Further heating is required to drive this off, resulting again in further darkening.

Various catalysts, or substances which speed up chemical reactions, hasten the development of rancidity, and the accompanying darkening of an oil. Both protein decomposition products and oil already rancid catalyse the rancidification of oil. Protein decomposition products, as already pointed out, result from spoilage of the fish between the time they are caught and the time they are processed. Contamination by rancid oil may result from using drums or tanks which have previously been used for the storage of fatty oils and have not been properly cleaned. Failure to clean containers which have previously contained fuel oil may also seriously affect the colour. Kniseley (1936) gives the curves (figure 8) of the effect of fuel oil on the red colour of herring oil. It can be seen that even as little as 0.01 per cent of fuel oil has a distinct effect.

Various metals can also catalyse the rancidification and darkening of fish oils. Of the metals used in plant construction, iron, lead and copper have this effect. In order that the metal be effective it must dissolve in the oil, and solution takes place more readily, in the first place, if the metal is in the form of an oxide, and in the second place, if the oil contains moisture or free fatty acid. The use of oxides, such as red lead in sealing pipe joints, should thus be avoided in plant construction. Briod and Christiansen (1930) have shown experimentally the extent to which a typical sample of market cod liver oil darkened when stored in contact with iron for three months. The darkening was accompanied by an

increase in the iron content of the oil. Dehydration of the oil had some retarding effect on this colour development, but removal of the free fatty acids followed by dehydration caused a more marked retardation. Thus the oils of better quality, which are low in moisture and free fatty acid, suffer less darkening as a result of contact with iron.

From the preceding discussion it can be seen that deterioration of the fish before processing, and careless methods of preparing and handling the oil, such as undue heating and the use of dirty containers, all cause darkening of the oil.
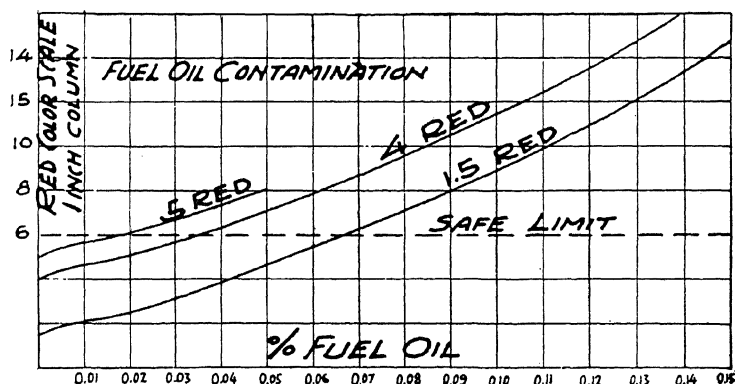
FIGURE 8. Effect of fuel oil on red colour of herring oil.

(d) REMOVAL OF COLOUR FROM FISH OILS

There are several physical and chemical principles which can be applied to the removal of the colour from fish oils. The most important are adsorption, extraction by immiscible solvents (solvents which will not dissolve the oil), oxidation and reduction. Although all of these are not used industrially, each has been successfully used in the laboratory to remove part or all of the colour from oils, and so they have possibilities of application on a larger scale. The technical methods which are now used in the industrial decolorization of oils are described in Section 8—under refining (1c).

Various solid materials have the property of concentrating other substances, particularly liquids, gases or substances in solution, at their surfaces. This phenomenon is known as adsorption. Since it is a surface effect, the activity of an adsorbent is not only a specific property depending on the particular material, but it is a direct function of the surface presented. In order to have a high surface per unit of weight a substance must be in a state of very fine division. This can be accomplished either by using a finely-powdered adsorbent, or by precipitating the adsorbent directly in the oil in the form of fine particles. Adsorbents belonging to both the above classes can be used to remove the colouring-matters

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from fish oils. Among the former there are various charcoals and "activated" earths which have been found suitable, while decolorization by alkali refining comes in the latter category. Alkali refining consists in neutralizing the free fatty acid of the oil with a concentrated solution of caustic soda or caustic potash, allowing the soap thus formed to settle out and drawing off the clear oil. While the soap formed appears to be liquid, it is actually in the form of very small particles suspended in the aqueous phase. These small soap particles are very powerful adsorbents for the pigments in the oil. The adsorptive effect of soaps is discussed in a later section.

While the separation of pigments by their distribution between immiscible solvents is used to a considerable extent in the study of natural pigments in the laboratory, the method has not found very great industrial application since some of the pigments are similar in their solubilities to the oil itself and cannot be thus separated from it. In industrial decolorization it is usually desired to remove all the colour, or as much of it as possible, not merely to separate certain individual pigments. There are, however, interesting possibilities of removing chlorophyll, the green plant pigment which is sometimes found in pilchard oil, from the oil by such a method on an industrial scale, since chlorophyll is soluble in 80 per cent acetone or 90 per cent alcohol, neither of which will dissolve the oil to any great extent.

Both the natural pigments of the oil and those developed in it after the time the fish was taken from the water can be removed by adsorption. Oxidation, on the other hand, will remove only the former. In bleaching an oil by oxidation, it is also necessary to exercise considerably more care than by the other methods since, if the process is carried too far, the oxidising agents will attack the oil itself, causing it to darken. Oxidation of the pigments may be carried out in various ways. An oxidising agent such as sodium or potassium hypochlorite, sodium or potassium dichromate, sodium or potassium permanganate or sulphuric acid can be used, in suitable concentration, or air can be blown through while the oil is kept at an elevated temperature.

When an oil is reduced the natural pigments are destroyed, owing to the fact that their colour depends largely on the presence in the molecule of a number of conjugated double bonds which are lost when the oil is hydrogenated or reduced by other means. Although reduction by hydrogenation is used to convert a liquid oil to a solid fat, considerable decolorization may be accomplished before the oil itself is changed to an appreciable extent, since the pigments are thus destroyed very rapidly by hydrogenation. Reduction apparently does not affect the pigments which have been developed in the oil after the time the fish was removed from the water.

It is inadvisable to decolorize an oil which is to be used as a source of vitamins since most methods of decolorization cause a loss of vitamins as well as of pigments. Oxidation and reduction are the most destructive. Drummond and Hilditch (1930) state that

"... we are strongly of the opinion that anything of the nature of 'blowing' of cod liver oil with a view to improving its appearance is bound to have a very detrimental result on the medicinal value of the product and may actually confer harmful properties on the oil.

"For practical purposes, therefore, we are left with the alternatives of removal of stearin and foreign matter by mechanical separation, and of improving the odour, flavour and colour, if necessary, by treatment with adsorbent materials such as Fuller's earth, silica gel, charcoal, etc. We feel that the ideal treatment would be merely to separate stearin and other material by chilling the oil and expressing the liquid portion, but we are also aware that, in some cases at all events, the product so obtained may be sufficiently strongly coloured and flavoured to render some further decolorizing and deodorizing treatment desirable."

III. OTHER NON-FAT COMPONENTS

(a) STEROLS

Sterols are solid fatty substances found in both animal and vegetable tissues. When purified they form small, greasy crystals, melting above the boiling point of water. They are insoluble in water but soluble in ether and most other organic solvents including oils, though only slightly soluble in cold alcohol. All of the various known sterols have a complex molecular structure including one secondary alcoholic group capable of esterification with fatty or other acids, and usually including one or more unsaturated bonds permitting hydrogenation or addition of bromine and other reagents. Individual sterols have been isolated in marine animal tissues, e.g. asterol and stellasterol from starfish, ostreasterol and stigmasterol from oysters and other molluscs, actiniasterol from sea anemones, and ambrein from the ambergris of the sperm whale. The only sterol occurring in appreciable quantities in marine animal oils, however, is *cholesterol* (accompanied by its esters).

Cholesterol ($C_{26}H_{44}CHOH$) has been reported as constituting up to 70 per cent of the unsaponifiable matter of halibut liver oil and as much as 35 per cent of the whole oil from moon-fish livers. There are several isomeric cholesterols but the one most frequently encountered forms silky, needle-like crystals melting at 150°C. when crystallized from non-aqueous solvents and small, waxy, plate-like crystals containing water of crystallization when crystallized from 80 to 90 per cent alcohol. Specific gravity, 1.067, iodine value 65.7. Its solubility in parts per 100 parts of solvent is 0.25 in cold water, 1.08 in cold alcohol, 11.0 in boiling alcohol, and it is much greater in ether, benzene, chloroform and other organic solvents. Despite its low solubility in water, true colloidal solutions and emulsified suspensions of cholesterol in water are readily formed. The one unsaturated bond in cholesterol is readily hydrogenated to yield β-cholestanol; the crystalline dibromide addition product of cholesterol (m.p. 123°C.) is used for identification and purification purposes. In the natural state, the secondary alcoholic function is frequently esterified by fatty acids such as oleic, palmitic and stearic. This same alcoholic function may be artificially esterified to form soluble sulphonates and other derivatives (page 20).

The presence of cholesterol may be detected by various colour reactions, e.g. a few drops of acetic anhydride and then a few of concentrated sulphuric acid added to a solution of cholesterol in chloroform produces a play of colours changing from red to bluish-green. Sulphuric acid and very dilute iodine solution give a somewhat similar play of colours in reverse order. An almost quantitative separation from saponified fats can be effected by an alcoholic solution of digitonin which forms an insoluble compound with cholesterol, but not with its esters.

It has been suggested that the presence of cholesterol and its esters in fish liver oils is due to a sequence of reactions involving biochemical transformations of the glyceride fats and hydrocarbons such as squalene.

The consumption of cholesterol or its esters in the quantities ordinarily secured through the medium of medicinal fish liver oils or fish oils for animal feeding has no undesirable effect on the organism (Kimizuka 1938).

The cholesterol content of very few Canadian fish oils has been actually determined. Experiments carried out in these laboratories showed a sample of Pacific coast grayfish liver oil to contain 5.1 per cent, and a sample of pilchard oil about 6 per cent in the unsaponifiable portions. Determinations of cholesterol performed elsewhere on other fish oils have yielded the following data:

	Cholesterol in whole oil (%)	Cholesterol in unsaponifiables (%)
Elasmobranch liver oils....................	....	8 to 16
Atlantic grayfish liver oil................	3	....
Gadid liver oils..........................	....	13 to 32
Cod liver oil.............................	0.3 (av.)	up to 50
Perch and carp liver oil..................	0.5 to 0.9	....
Sperm whale head oil.....................	0.2	....

The liver oil in the basking shark has been investigated by various workers whose data on the cholesterol content differ widely. From 4 to 22 per cent cholesterol in the whole oil, and from 1 to 20 per cent cholesterol in the unsaponifiable matter have been independently reported. It has been estimated that 90 per cent of the cholesterol is esterified with fatty acids, and that 26 per cent of the total amount of fatty acids in some basking shark liver oils is in combination with cholesterol.

In an extensive investigation of the relation between the percentages of unsaponifiables in various Atlantic fish livers and the sterol contents of the unsaponifiable matter (Channon 1928), some significant features were exhibited:

	Unsaponifiables in liver oils (%)	Sterols in unsaponifiables (%)
Elasmobranchii....................	1.1 to 81.5	72.6 to 0.1
(sharks, skates, rays)	(av. 25.8)	(av. 32.9)
Teleostomi........................	0.1 to 2.4	83.5 to 42.9
(whiting, cods, hake, plaice, sole, etc.)	(of liver weight)	(av. 63.3)

In the case of the Elasmobranchii, where the greatest ranges were found, the sterol contents in general were highest when the total amount of unsaponifiables was lowest. All sterol contents below 8 per cent were confined to the one family Squalidae (including the Atlantic grayfish) in which the highest percentages of unsaponifiables were found.

Elasmobranch liver oils can be arranged in groups in which the unsaponifiable content, when small (1 to 2 per cent), consists chiefly of sterols. A study of nine species of Japanese elasmobranchs showed that, for widely differing

species, the ratios of cholesterol to total unsaponifiables and of vitamin A to total unsaponifiables varied between narrow limits.

From the standpoint of the possible commercial importance of marine sources of cholesterol, attention has been drawn to the fact that oil from American shrimp waste yielded 19 per cent of cholesterol, and Abernethy and Vilbrandt (1931) have estimated that 80,000 lb. of cholesterol could be recovered from an average year's waste in the southern United States shrimp industry.

The solubility of cholesterol in hot alcohol and its precipitation from cold alcohol is in general a means of separating cholesterol from many other constituents of unsaponifiable matter. Patents for recovering cholesterol directly from fats and oils without risking emulsification by the soaps include U.S. patent 1,610,854 (treatment of the fat with successive amounts of alkali inadequate for complete saponification, removal of the soaps so formed, and a final careful saponification of the small amounts of remaining glycerides); German patent 508,407 (treatment of the saponified fat by a special soap prepared from cocoanut and/or palm-nut oil, diluting the mixture, and allowing it to stand in the warm after saturating it with salt); and Dutch patent 29,780 (distillation of unsaponifiable under high vacuum and pouring the higher-boiling fractions into a cold mixture of equal parts of acetone and methyl acetate. On cooling to room temperature the cholesterol crystallizes out). U.S. patent 1,548,216 describes an improved method for the recovery of cholesterol from spermaceti by saponification of the waxes with sodium ethylate.

Cholesterol is closely related to vitamin D. When crude cholesterol of animal origin is irradiated with ultraviolet light it becomes antirachitic and is equally effective on rats and chickens. (The irradiation of ergosterol, discussed in part I of this section, produces an antirachitic substance more active towards rats than towards chickens). However, only a small fraction of such crude cholesterol can be activated by irradiation and for some time it was considered that the provitamin was ergosterol. This is now known to be erroneous, since highly purified cholesterol, definitely free of ergosterol, can be activated by ultraviolet light (Bethke *et al.* 1937), although only to a slight extent. The activatability of cholesterol is enhanced by heating in the presence of oxygen before irradiating. The irradiation products of both the non-heated and heated cholesterol resemble the vitamin D of cod liver oil in that they are equally efficient on rats and chickens. The irradiation of a substance known as 7-dehydrocholesterol (identical with cholesterol except that it lacks two hydrogen atoms) produces an antirachitic substance known as vitamin D_3 that is identical with the natural vitamin D in fish liver oils. It is therefore suggested that, during irradiation of cholesterol, some dehydrocholesterol is formed and this substance is the actual precursor of the active vitamin. Other treatments that enhance the activatability of cholesterol may also produce this dehydrocholesterol as an intermediate product. Cholesterol may also be activated by purely chemical means but the products are not as active as those obtained by irradiation; some of such treatments include adsorption on fuller's earth, heating with various metallic salts such as acid potassium sulphate, copper sulphate, zinc or aluminium chlorides. Milas and Heggie (1938) increased the activatability of cholesterol by treatments that favoured the formation of 7-dehydrocholesterol. United States patent 2,112,200 covers such a process involving the distillation of the cholesterol with benzoyl peroxide and mercury in a vacuum, then irradiating.
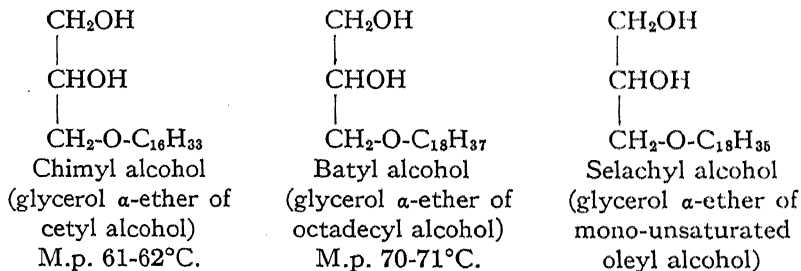
Four additional applications of cholesterol in therapeutics are: the use of a mixture of cholesterol and chaulmoogric oil or the chemical compound of cholesterol with chaulmoogric acid for the treatment of leprosy; the combination of vitamin A with cholesterol for tuberculosis therapy; German patent 514,095 on the preparation of cholesterol phosphates for pharmaceutical purposes, and its use for stabilizing suspensions of drugs to withstand sterilization before injection; British patent 328,922 on the preparation of colloidal solutions of cholesterol by dissolving it in chloroform and diluting the solution in aqueous alcohol.

The fact that cholesterol so readily emulsifies with water in the presence of soaps, saponins, lecithin, etc., gives it considerable application in the cosmetic industry, since cholesterol definitely plays a decided role in skin and scalp health. Sebum, the principal fat in sweat, is a secretion for the skin's protection and consists in general of cholesterol esters of fatty acids. Artificial cholesterol esters do not emulsify with water and soaps to the same extent as does cholesterol, but these esters have the property of mixing with enormous quantities of water yet retaining their fatty consistency (e.g. "lanoline"). Cosmetics employ varying quantities of cholesterol, from one per cent in a typical anti-wrinkle cream to larger amounts in special ointments. It is claimed that irradiated cholesterol in creams is absorbed through the skin without the ill effects such as formation of calcium deposits thought to be produced by some other irradiated products.

Crude cholesterol materials are purified by heating and agitating with nitric acid at 140 to 250°F. The resulting wax-like or viscous substance is suitable for leather dressings, waterproofing, water- and acid-proof packing and joints, etc. (British patent 170,241). Leather dressers state that Canadian salmon oil used in their trade should contain a certain amount of cholesterol and that the amount in some salmon oils is insufficient. The cholesterol presumably hinders "spueing". Cholesterol can be used in the "suint" and rubber resins of importance for the waterproofing of military clothing, and sulphonated cholesterol has possibilities in the textile industries as a softener. When heated with certain clays under ordinary pressure, cholesterol decomposes to give hydrocarbons.

(b) GLYCEROL ETHERS

The presence of three new alcohols in the unsaponifiable portion of elasmobranch liver oils was first noted in 1922, but it was not until some six years later than the ether nature of these was recognized. They were later shown to have the constitution:

CH_2OH	CH_2OH	CH_2OH
$CHOH$	$CHOH$	$CHOH$
CH_2-O-$C_{16}H_{33}$	CH_2-O-$C_{18}H_{37}$	CH_2-O-$C_{18}H_{35}$
Chimyl alcohol	Batyl alcohol	Selachyl alcohol
(glycerol α-ether of	(glycerol α-ether of	(glycerol α-ether of
cetyl alcohol)	octadecyl alcohol)	mono-unsaturated
M.p. 61-62°C.	M.p. 70-71°C.	oleyl alcohol)

A fourth ether, skesyl alcohol (m.p. 64-65°C.), has recently been reported which appears to be the glycerol ether of the myristyl alcohol $C_{14}H_{29}OH$.

The two remaining alcoholic functions of these glycerol ethers appear to be esterified with fatty acids to some extent in the natural oil, but as yet no definite statement can be made as to which acids are combined with the different glycerol ethers since these acids are split off during the isolation of the unsaponifiable matter. The acids are probably of the usual saturated and unsaturated types found in liver oils.
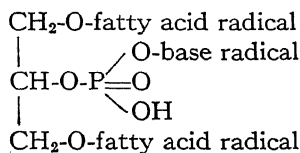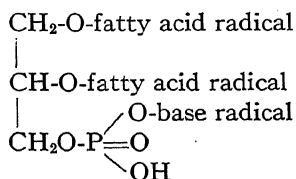
Although the 30 per cent of unsaponifiable material in the liver oil of the ratfish (*Hydrolagus colliei*) has been reported to consist almost entirely of a mixture of chimyl, batyl and selachyl alcohols (Lovern 1937) and the whole, unsaponified (liver?) oil of the shark (*Scymnorhinus lichia*) is said to contain 21.3 per cent of fatty acid esters of these alcohols, they are not, in general, an important constituent of marine animal oils. From a nutritive standpoint they have neither growth-promoting nor antirachitic properties and their function in the animal organism is still obscure.

Little commercial significance has been attached to batyl, chimyl and selachyl alcohols; it has been stated that they form suitable raw material for the manufacture of wetting-out agents, through the ability of at least the primary of the two free alcoholic groups to undergo sulphation or sulphonation (British patent 398,818). Hydrogenation of oils containing esters of selachyl alcohol would tend to convert these esters into saturated esters of the saturated batyl alcohol.

Few data on the content of batyl, chimyl and selachyl alcohols in Canadian fish oils are on record. In the course of an unpublished investigation at this Station, the unsaponifiable portion of one sample of British Columbia grayfish liver oil (*Squalus sucklii*) was shown to contain about 10 per cent of batyl and selachyl alcohols. Two, and sometimes all three of these alcohols or their esters are found in the liver oil of various species of sharks known to inhabit Canadian waters, as well as in the liver oils of skates and rays. The unsaponifiable material in the liver oil of a member of the family Gadidae (which includes some cods) has been reported to contain a trace of batyl alcohol.

(c) PHOSPHOLIPIDES

The phospholipides are described at this point since, although they are glycerides and resemble the fats in their physical properties, they are not true fats. Their constitution (as given here) shows them to be formed from glycerol by two of its alcoholic groups being esterified with fatty acids, and the third esterified with the inorganic acid, phosphoric acid, which in turn is partially esterified with an organic base. The nature of this base radical determines the name and properties of the phospholipide. On saponification, the glycerol, fatty acids, phosphoric acid and organic base produced are all soluble in the alkaline saponifying medium and, therefore, do not contribute to the unsaponifiable portion of the oil containing the phospholipide.

$$
\begin{array}{ll}
\text{CH}_2\text{-O-fatty acid radical} & \text{CH}_2\text{-O-fatty acid radical} \\
\quad | & \quad | \qquad \diagup\text{O-base radical} \\
\text{CH-O-fatty acid radical} & \text{CH-O-P}\!\!=\!\!\text{O} \\
\quad | \qquad \diagup\text{O-base radical} & \quad | \qquad \diagdown\text{OH} \\
\text{CH}_2\text{O-P}\!\!=\!\!\text{O} & \text{CH}_2\text{-O-fatty acid radical} \\
\qquad \diagdown\text{OH} &
\end{array}
$$

The only phospholipide occurring in any appreciable quantity in marine animal oils is *lecithin*, in which the base designated in the above formulae is the

nitrogenous alcohol *choline*, HO-CH$_2$-CH$_2$-N(CH$_3$)$_3$-OH. Actually, several different lecithins may be present since the phosphorus may be linked to the glycerol in either of the two ways shown above, and the nature of the fatty acids may vary widely to include saturated palmitic, stearic, etc., and unsaturated oleic, linoleic, linolenic, etc., acids.

"Pure" lecithin is a waxy, white solid which changes on exposure to light and atmospheric oxygen to a yellowish or brown substance. It readily absorbs moisture forming a soft, greasy, plastic mass. It has no definite melting point, but softens at 60°C. and decomposes to a brown substance at 110°C. It dissolves very easily in alcohol, ether, chloroform, benzene and light petroleum, but not in acetone. It will, however, dissolve to some extent in acetone containing fats or fatty acids. Although actually insoluble in water, sufficient contact with water causes it to swell and ultimately form a slimy emulsion or colloidal solution. This property, and its further property of acting as an emulsifying reagent for preparing colloidal solutions of proteins in organic media, give lecithin some commercial importance.

During saponification of a marine animal oil, lecithin is deprived of its fatty acids and at least part of the choline, and it is probable that part, if not most, of the residue may have gone into solution or an emulsified state in the aqueous saponifying liquid. If saponification is complete, the resulting fatty-acid soaps, alkali glycerophosphate and choline or its breakdown products are all far more soluble in water than in the ether used for separating the unsaponifiables.

Lecithin was recognized in the roe of fish as early as 1857. Few data on the lecithin content of Canadian fish oils are available; the content in chum salmon egg oil was found in these laboratories to be approximately 18 per cent. The oil from dogfish (grayfish) eggs has been found to contain about 12 per cent, and an Argentine shark was reported to contain 13.4 and 7 per cent lecithin in the liver and spawn respectively. A German whale oil contained 4.3 to 6.4 per cent, and small amounts in the ovaries and testes of tuna and in salmon, cod, carp, halibut, herring and shark eggs have been detected. The lecithin fatty acids of Japanese herring roe are chiefly palmitic, oleic, linoleic and linolenic. Fifteen species of north Atlantic sea fish showed the whole fish to contain only 0.1 to 0.7 per cent lecithin.

The amount of phospholipides or lecithin in fish oils is best calculated from an analytical determination of the phosphorus that characterizes these compounds. The separation of lecithin from an oil in good yield is a difficult matter, one method being based on the insolubility of this compound (as compared with the fats, cholesterol, etc.) in acetone.

Lecithin is used in the chocolate, cosmetic, margarine, soap and other industries employing fats. These uses include the prevention of "blooming" in chocolates, and the stabilization of emulsions, particularly of the water-in-oil type used in cold creams and cleansing creams. Since lecithin can be obtained for commercial purposes from many sources (e.g. egg-yolk) other than marine animal tissues and oils, it is doubtful whether its presence in such oils is of commercial significance. Its natural occurrence in cod liver oil (sometimes fortified by the addition of extra amounts) has been utilized in the preparation of the well-known cod liver oil emulsions.

(*d*) WAXES AND FATTY ALCOHOLS

Marine animal waxes are fatty acid mono-esters of fatty alcohols (page 18) and are therefore chemically distinct from the fats and fatty oils which they

superficially resemble. Wax is here used in its chemical sense, for some marine animal waxes are liquid at room temperatures. The term is rather loosely applied to other types of compounds which are not true waxes; e.g. paraffin "wax" is a hydrocarbon and Japan "wax" is actually a fat.

The chief source of marine animal waxes is the oil found in the head cavities of the sperm whale, though waxes may also be isolated from the head or blubber oil of most other species of marine mammals and in small quantities from the oils of some fishes. Sperm-whale head oil is liquid at the body temperature of the animal, but becomes semi-solid on cooling owing to the separation of a mass of fine crystals. By chilling to about 0°C. and pressing to remove the residual oil, some 12 per cent of the original oil is recovered as a crystalline substance retaining a wax-like consistency at 15°C. This material is the *spermaceti* of commerce and consists of a mixture of true waxes, the chief constituent being cetyl myristate (the ester $C_{13}H_{27}CO.O.C_{16}H_{33}$ from myristic acid $C_{13}H_{27}COOH$ and cetyl alcohol $C_{16}H_{33}OH$).

Analogous to the complexity of naturally occurring fats, the waxy portion of a marine mammal oil consists of a mixture of several or many chemically different waxes. Thus commercial spermaceti contains in addition to cetyl myristate, variable proportions of cetyl laurate, cetyl palmitate and other waxes as well as small amounts of true fats. Sperm-whale head and blubber oils have been demonstrated to contain waxes consisting of saturated fatty acids having 12, 14, 16, or 18 carbon atoms (see table I), or mono-unsaturated fatty acids having 12, 14, 16, 18, 20, or 22 carbon atoms (see table II), esterified with one of the fatty alcohols listed in table XVI.

The waxes are all insoluble in cold or hot water, but dissolve in hot alcohol and in most organic solvents such as ether, chloroform and benzene. When pure, they are colourless liquids or white waxy solids, lighter than water, and do not form films on exposure to air or become rancid, although commercial spermaceti may turn brownish and acquire a rancid odour after long exposure to light and air, due to the presence of impurities. Waxes are in general much more difficult to saponify than are the fats; the resulting alcohols, unlike the glycerol from fats, are insoluble in water and thus hinder access of the saponifying agent to the remaining unsaponified material. Spermaceti requires refluxing for one hour with 15 per cent alcoholic alkali for complete saponification whereas most fats would be saponified by this reagent in half an hour.

Since waxes such as the various grades of spermaceti are mixtures of several individual esters, their physical constants are best expressed between limits. Thus, spermaceti may have a specific gravity of from 0.945 to 0.960 at 20°C. (0.808 to 0.816 at 99°C.) and a melting point of from 40.5 to 47.2°C. Chemically individual waxes are difficult to isolate from the naturally occurring substances, but may be prepared synthetically. The melting points of a few synthetic waxes from saturated constituents are as follows: lauryl laurate, 21.1°C.; cetyl palmitate, 55.5°C.; stearyl laurate, 37.2°C.; stearyl palmitate, 59.4°C.; cetyl myristate, 50.5°C.; and cetyl stearate, 60.5°C. Unsaturation in either the fatty alcohol or

fatty acid constituent considerably lowers the melting point, giving rise to waxes that are liquid at ordinary room temperature.

Liquid marine animal waxes from the sperm and Arctic sperm whale were at one time in considerable use as fuels for heating and lighting purposes, but are now used for their excellent lubricating characteristics in connection with light machinery, due to their non-gumming property and their relatively slight decrease in viscosity with rise of temperature.

Solid marine animal waxes (commercial spermaceti) are used in candle manufacture, for superfatting soaps, and as a constituent (up to 10 per cent) of various cosmetics such as cold creams and face creams.

Fatty alcohols may be prepared, as indicated above, by the saponification or hydrolysis of marine animal waxes, and are also reported as existing in the free state in some marine oils; sperm-whale head oil has been reported to contain cetyl alcohol and appreciable amounts of oleyl alcohol, the latter being also present in small amounts in certain fish liver oils. The fatty alcohols are colourless liquids or white microcrystalline solids with practically no odour and a slightly greasy feel. They are lighter than, and insoluble in, water but soluble in alcohol and most other organic solvents. Some of those that have been reported as occurring free or in combination in marine animal oils are shown in table XVI.

Cetyl alcohol is the principal fatty alcohol prepared commercially by the saponification of marine waxes. The original oil, containing both fats and waxes, is first subjected to a saponification process that leaves unaltered the more difficultly saponified waxes which are recovered

TABLE XVI. Fatty alcohols of marine animal origin

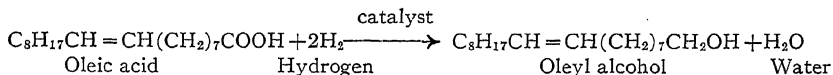| Name	Formula	Melting point (°C.)	Boiling point (°C.)	Specific gravity
Saturated alcohols				
Octyl............	$C_8H_{17}OH$	−16	195	0.827
Decyl............	$C_{10}H_{21}OH$	7	231	0.830
Lauryl (lethal)....	$C_{12}H_{25}OH$	24	255	0.831**
Myristyl (methal).	$C_{14}H_{29}OH$	37	167*	0.824**
Cetyl (ethal)......	$C_{16}H_{33}OH$	49	344 } 190* }	0.818**
Stearyl (stethal)...	$C_{18}H_{37}OH$	59	210*	0.812**
Unsaturated alcohols				
Atrophyl.........	$C_8H_{15}OH$	liquid	95*	0.826
Macrocephalyl....	$C_{10}H_{19}OH$		101*	0.834
Odontocetyl......	$C_{12}H_{23}OH$		157*	0.840
Physeteryl.......	$C_{14}H_{27}OH$			0.847
Zoömaryl........	$C_{16}H_{31}OH$			0.850
Oleyl............	$C_{18}H_{35}OH$		209*	

*At a pressure of 15 mm. of mercury.

**At temperature just above the melting point.

from the colloidal soap solutions by filtration, centrifuging or decantation. German patent 656,215 (1938) describes the use of a lipase enzyme for the selective hydrolysis of the fats. The separated waxes are then subjected to more vigorous saponification (e.g. action of concentrated aqueous alkali at 300 to 570°F. for 4 hours) and the liberated cetyl alcohol is recovered from the soaps of the fatty acids by distilling at 645°F. or at a lower temperature under reduced pressure. The selective action of certain solvents such as petroleum spirit for cetyl alcohol may alternatively be used to effect the separation.

Certain of the fatty alcohols listed in the above table, as well as others not occurring combined in marine waxes, are now being manufactured commercially in large quantities from several materials (including the fatty acids and fats of marine oils) by various chemical processes. Such processes include the following:

(1) The direct hydrogenation of free fatty acids, their methyl esters or glycerides, by special mixed catalysts. United States patent 1,839,974 is the most detailed of the earlier patents for such hydrogenation, and a recent review by Mullin (1938-1939) discusses subsequent developments. The hydrogenation can be so controlled as to leave unaltered the unsaturated double bonds in the carbon chain:

$$C_8H_{17}CH = CH(CH_2)_7COOH + 2H_2 \xrightarrow{\text{catalyst}} C_8H_{17}CH = CH(CH_2)_7CH_2OH + H_2O$$

$$\text{Oleic acid} \qquad \text{Hydrogen} \qquad \text{Oleyl alcohol} \qquad \text{Water}$$

(2) The reduction of fatty acid esters by hydrogen generated from metallic sodium and an alcoholic solvent. The fatty acids of sperm oils have been thus converted into fatty alcohols (United States patents 2,070,318; 2,070,597; 2,075,963). (3) The oxidation of hydrocarbons either directly to fatty alcohols, or to fatty acids which are then hydrogenated as described.

By means of these or other processes a fatty alcohol corresponding to each of the fatty acids, listed in tables I and II as occurring in marine animal oils, could be prepared. The properties of such alcohols not included in table XVI may be estimated from the data there presented, which indicate the effects of length of carbon-atom chain and presence of unsaturation. The alcohols melt at temperatures 10 to 20°C. lower than the corresponding acids, and also possess lower boiling points and specific gravities.
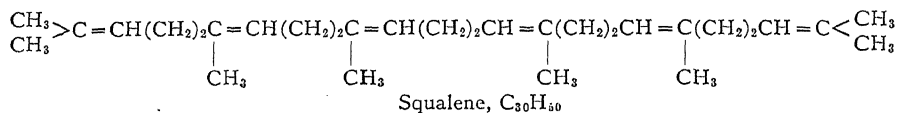
Natural and synthetic fatty alcohols have recently achieved considerable importance in many technological fields. Owing to their physical properties and chemical stability including lack of tendency towards rancidity, they are used extensively in cosmetic preparations. Other important uses include the manufacture of polishing compounds, defoaming agents, special soaps, pharmaceutical products such as perfumes and coatings for tablets, lubricants and improvers for drying oils; as emulsifiers they allow production of creams of both the water-in-oil and oil-in-water types, and when sulphated or sulphonated (pages 136, 140) form other valuable detergents and emulsifying agents, particularly for the fur and leather industries. Commercial fatty alcohols are usually mixtures that have been distilled under reduced pressure and which go under various trade names such as: "Lorol" (technical lauryl alcohol), a mixture of decyl, lauryl and myristyl saturated alcohols, with lauryl predominating; "Ocenol" (technical oleyl alcohol), a mixture of unsaturated C_{16} and C_{18} acids, with oleyl (C_{18}) predominating; and "Lanette wax" (technical stearyl alcohol), a mixture of cetyl and stearyl saturated alcohols.

(e) HYDROCARBONS

Hydrocarbons in marine animal oils were first recognized by Tsujimoto (1906) and later received some prominence when a shipment of Atlantic grayfish liver oil from Lisbon was refused in London on the grounds of alleged adulteration with

neral hydrocarbon oils. Further examination disclosed that the hydrocarbons
:re natural constituents of the liver oil. It is now recognized that hydrocarbons
ɔy constitute 90 per cent or more of the unsaponifiable material of certain shark
'er oils.

The principal hydrocarbon present in the liver oils of fish belonging to the shark family
s been shown to be highly unsaturated and is known as *squalene*. Its structure, as proved
 synthesis, reveals the presence of six unsaturated bonds per molecule:

$$CH_3{>}C=CH(CH_2)_2C=CH(CH_2)_2C=CH(CH_2)_2CH=C(CH_2)_2CH=C(CH_2)_2CH=C{<}CH_3$$

$$\underset{CH_3}{|}\qquad \underset{CH_3}{|}\qquad\qquad \underset{CH_3}{|}\qquad\qquad \underset{CH_3}{|}$$

Squalene, $C_{30}H_{50}$

is a colourless liquid solidifying to a white wax at about $-75°C$. Under ordinary pressure
boils at $330°C$. accompanied by some decomposition, though it can be distilled at reduced
essure without decomposition. It is insoluble in water, slightly soluble in cold alcohol, and
adily soluble in most other organic solvents; its specific gravity is 0.86. By hydrogenation
is converted into the corresponding saturated hydrocarbon, squalane, also a liquid. With
'drogen chloride, squalene forms a crystalline hexahydrochloride melting at $144\text{-}145°C$., which
:rves for identification and purification purposes; it may also be recognized by the blue colour
·oduced when squalene is warmed with a sulphuric acid solution of phosphomolybdictungstic
:id (Sabetay 1938).

Since the first description of squalene several other hydrocarbons have been
ɔported in marine animal oils. There has been some doubt concerning their
ʝentity and composition and possibly different investigators have given different
ames to the same compound, as in the case of spinacene, which for years after
: was first described by Chapman (1917) was considered a separate compound
.ntil it was finally shown to be identical with squalene. Some of these more or
ɔss definitely characterized hydrocarbons are listed below. With the exception
·f pure pristane, which melts at about $30°C$., they are liquids at ordinary temper-
.tures with a specific gravity of about 0.8.

IYDROCARBONS OF FISH LIVER OILS

Name	ʔormula	No. of unsaturated bonds	Theoretical iodine value	Occurrence
Ɔecane	$C_{10}H_{22}$	0	0	shark
ᵖristane.....	$C_{18}H_{38}$	0	0	shark
ɔamene.....	$C_{18}H_{36}$	1	101	basking shark
Ɔadusene...	$C_{18}H_{32}$	3	307	cod
Ɔetorhinene.	$C_{28}H_{46}$	6	398	basking shark
Ɔqualene....	$C_{30}H_{50}$	6	371	various fish

Hydrocarbons having possibly eight unsaturated bonds are reported as occurring
in the unsaponifiable material from the liver oil of a Japanese sea perch; and two
unsaturated hydrocarbons, $C_{13}H_{14}$ (orange red crystals melting at $105°C$.) and
$C_{14}H_{16}$ (red crystals melting at $126°C$.), probably of the naphthalene hydrocarbon
type, are stated to occur in the unsaponifiable portion of a Japanese cod liver oil.

The origin of hydrocarbons in marine animal oils does not appear to be
directly related to the nature of the food ingested by the fish. No squalene could

be found in samples of the plankton on which many fishes feed, and the irregular distribution of hydrocarbons in the species of fish feeding on other fishes would indicate that these hydrocarbons are synthesized for some as yet unrecognized purpose in most Elasmobranchii (principally the family Squalidae, including the grayfishes) but only in very small amounts or not at all in the Teleostomi. One species of *Squalus* having 35.6 per cent squalene in the liver oil was reported to contain none in the oil from other parts of the body, but other investigators have demonstrated its presence in fish egg oils, in the unsaponifiables of sperm whale blubber oil, and in the peculiar reservoir of oil found in the stomach of the small shark *Scymnorhinus lichia* and used by fishermen as fuel for their lamps. Over one half of this oil is unsaponifiable matter containing 98 per cent of squalene.

Hydrocarbons in oils from Canadian fishes have been but little investigated. Squalene was found in very small amounts in Newfoundland cod liver oil (Drummond and Baker 1929) and an investigation by Percival (unpublished) at our Nanaimo Station indicated that the major portion of the unsaponifiables in British Columbia grayfish liver oil consisted of squalene. In general, squalene is found chiefly in fish liver oils having a high content of unsaponifiables, though the converse is not necessarily true (Channon 1928). Basking-shark liver oil often contains about 50 per cent of unsaponifiable matter, one-quarter to one-third of which consists of squalene and other hydrocarbons such as pristane. But, except for the basking shark, the smaller sharks (including the grayfishes) appear to contain the greatest amounts of hydrocarbons; squalene has been reported as absent in the liver oils of the sleeper, blue and whale sharks.

When the squalene content of shark livers is high, the degree of unsaturation in the fatty acids of the oils is low and there are large amounts of C_{24} acids; as the squalene content decreases, unsaturation of the C_{20} and C_{22} acids increases and the C_{24} acids tend to diminish in quantity.

Squalene administered to rats and rabbits does not give rise to any evident harmful effects. Its action on man has not been fully investigated, but it appears to be harmless, having little nutritive value. No antirachitic properties have been observed, even after irradiation with ultraviolet light; but when biochemically activated, it is reported to be effective in the cure of tuberculosis. It is of interest to note that squalene-containing fishes are remarkably free from parasites and other ills.

The possible utilization of squalene in the industrial arts has received considerable attention by various investigators. It absorbs atmospheric oxygen to the extent of 24 per cent of its weight in 28 days when exposed in a thin film, but the general conclusion reached has been that squalene is unsuitable as a constituent of paints. Its low solidifying point and viscosity characteristics (Ostwald viscosimeter—14.3 at 59°F.; Engler—2.4 at 77°F.; Redwood—91 seconds at 59°F. and 78 seconds at 70°F.) make it a good lubricant, and the above properties combined with its high boiling point and concomitant low vapour pressure have led to its being recommended as a supplying agent for organic plastic materials, carrier for perfumes, and for filling thermometers; French patent 823,767 and United States patent 2,169,192 cover the production of hydrocarbons from fish liver oils by distillation under very low pressures for these and other purposes.

French and Spanish investigators have claimed that shark liver oils, principally because of

:ir high hydrocarbon content, form suitable fuels for Diesel motors. The power obtained is
uivalent to that of Diesel oil, and operation is more flexible. In this connection, it may be
:ntioned that squalene has a flash point of 383°F., an ignition point of 473°F., and a calorific
lue of 19,400 B.T.U. per pound as compared with 18,900 to 20,000 B.T.U. for petroleum.
ualene has also been recommended as an anti-knock standard for gasoline engine performance.

The complete hydrogenation of squalene to squalane has already been mentioned. The
:ter is readily soluble in ether, gasoline and benzene, though only slightly soluble in alcohol
.d acetone; specific gravity, 0.8115 at 59°F.; viscosity (Ostwald), 36.9 at 59°F., (Redwood) ·
:1 seconds at 59°F.; flash point, 374°F. Its use as a lubricant and high grade insulating or
ansformer oil has been suggested. The properties of the products formed at each of the six
eps during hydrogenation of squalene to squalane have been studied by Heilbron *et al.* (1926).
y processes similar to the cracking of petroleum, with or without the presence of hydrogen,
ualene and squalene-containing fish oils have been broken down to produce good yields of
mpler hydrocarbons including petroleum spirit (59 per cent), kerosene (28 per cent) and residual
:avy oils. High-boiling terpenes, and naphthenic and other aromatic hydrocarbons can be
·oduced under other conditions.

British patent 345,734 describes the use of halogenated squalene for condensation with
:her substances to form dyestuff intermediates, and American patent 1,991,999 mentions the
ᴈe of squalene hexahydrochloride as an intermediate in the manufacture of retarding agents
)r rubber vulcanization. The squalene molecule is comprised of units closely resembling the
.oprene units of rubber and it is conceivable that isomerization and condensation of squalene
ᴐ form elastic substances may be possible.

British patent 354,417 and American patent 1,961,683 describe the treatment of squalene
r squalene-containing oils with an excess of a sulphating or sulphonating reagent to form
·roducts suitable as emulsifying agents in the textile, rubber and other industries. Attempts
t sulphurization led only to viscous liquids.

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SECTION 4.   METABOLISM OF FATS

The term metabolism is usually used to signify the chemical changes that occur in the living organism.   The various stages occurring in the metabolism of fats may be conveniently divided into the following processes: digestion, absorption, transport, utilization, storage and excretion.

Fat in the animal organism is from the fat in the food or is formed from surplus carbohydrate and protein.   Fat is the richest source of energy of any known foodstuff, yielding 9.3 calories per gram as compared to 4.1 calories per gram from carbohydrate and protein.   It usually occurs in a relatively dry state and is the main vehicle for the intake of the fat soluble vitamins.

I. PROCESSES OF METABOLISM

The digestion of fat begins in the stomach, where it tends to be limited, owing to the acidic nature of the gastric juice; the fat splitting enzymes in this medium are relatively inactive.   It has been shown by Ivy (1937) that neutral fat tends to inhibit gastric secretion and the motility of the stomach.   The chief process occurring in the stomach is the liberation of fatty material from protein through the action of the protein-hydrolyzing enzyme pepsin.   The ingested fat leaves the stomach and enters the small intestine as large drops or as solid masses in the case of fats of high melting-point.   The fat becomes emulsified in the intestine and is subjected to the influence of (a) the lipase of the intestinal juice, and (b) the lipolytic enzyme steapsin of the pancreatic juice.   The action of these enzymes is to hydrolyze the fat into fatty acid and glycerol.   The activity of the enzymes is considerably enhanced by a secretion from the liver known as bile, which enters the intestine in close proximity to the pancreatic duct.   Bile contains the salts of taurocholic and glycocholic acids, sodium carbonate, calcium salts and mucin-like substances, each of which is considered to play a role in the digestion and absorption of fats.   The special property of bile, in lowering the surface tensions of solutions and thus permitting a more ready flow of substances across a membrane, is noteworthy in this instance in the assistance it gives in the absorption of the relatively water-insoluble fatty substances through the intestinal wall.

Various theories have been advanced to explain the chemical changes taking place in the digestion and absorption of fats; none of them thus far, however, has adequately explained the process.   One of the older theories (advanced by Pflüger) considered that the lipase split the fat into fatty acids and glycerol, whence soap was formed by the reaction of the fatty acids with the sodium carbonate secreted with the bile.   These soluble soaps and glycerol diffused through

the intestinal wall where fat was resynthesized from the soap and glycerol. This theory is comparable to the process taking place with carbohydrate and protein digestion, in that the ingested foodstuffs are hydrolyzed into simpler and more diffusible substances which are more readily absorbed. The main objection to this theory is that the contents of the intestine of most mammals as well as man are not sufficiently alkaline for the formation of soaps. The soaps of the higher fatty acids are only stable in solutions at a pH of 8 or greater, and the intestinal contents are rarely above pH 7. The bile and pancreatic juice are alkaline in reaction, but when these secretions become mixed with the partly digested foodstuffs and gastric juice, the resulting intestinal contents are usually slightly acidic. It is possible that a local alkalinity may exist around the emulsified fat and in this way keep the soap in solution until absorption takes place. Another theory of fat absorption advanced by Verzar (1933) is based on the hydrotropic effect of bile salts. Verzar has shown histologically that fatty acids are absorbed as such and not as soaps. He claims the bile salts combine with the fatty acids, forming a complex aggregate which is readily diffusible and stable within the pH range of the intestines. However, Irwin *et al.* (1936) were unable to find any effect on fat absorption by the administration of small amounts of bile salts or other hydrotropic substances to normal rats, and the administration of large amounts of these substances tended to decrease the rate of absorption of fats.

Sinclair (1929) claims that one of the first steps in the resynthesis of fat after absorption is through the formation of phospholipides. Support to this idea is given by the results of the administration of iodoacetic acid and phlorizin to animals; these substances are believed by some workers to inhibit the phosphorylation of compounds *in vivo*. There is also evidence to show that the adrenal cortical hormone plays a role in fat absorption. It has been found that fatty acids diffuse through the cells of the intestines, but are not resynthesized into fat in the adrenalectomized rat, and the administration of the hormone to these animals corrects the deficiency (Verzar and Laszt 1935).

The size of the fat particles does not appear to be a factor in fat absorption according to Holt *et al.* (1933), who found that unemulsified butter in milk was quite as well absorbed in infants as the fat of homogenized milk.

The rate of fat absorption varies with the nature of the fat according to Steenbock *et al.* (1936); butter fat, halibut liver oil and cod liver oil were absorbed more rapidly than corn oil, lard and partially hydrogenated vegetable oils. It was also indicated that the unsaponifiable matter was absorbed more slowly than the glycerides.

Most workers agree that a small amount of fat is absorbed directly from the intestine into the blood stream and passes to the liver by way of the portal vein; however, the major portion (60 per cent at least) is absorbed into the lymph system and reaches the circulation by way of the thoracic duct. According to Hughes and Wemmer (1935) the short-chain fatty acids, e.g. those in butter, tend to be absorbed in a manner similar to non-fatty material, since they were unable to find any increase in the amount of soluble volatile fatty acids in the

thoracic lymph after feeding butter. After a fatty meal there is an increase in the blood fat of most mammals, particularly the carnivora; on the other hand the increase is not so readily detected in the herbivora and it is believed there is a more gradual absorption of fat in these animals.

The conversion of dietary carbohydrate into fat *in vivo* has been quite well established, although the mechanism of the change is not readily explained. The synthesis of fat from protein is a controversial subject whose mechanism is clothed in mystery. It has been demonstrated that certain amino acids can be converted into carbohydrate and this in turn may be converted into fat. Anderson and Mendel (1928) have shown that the ingestion of carbohydrate tends to produce a fat less unsaturated and with a higher melting point than those produced by the ingestion of most fats in feeds of vegetable origin.

In the utilization of the absorbed fat there are a number of paths it may take—(*a*) it may be oxidized at once with the liberation of energy, (*b*) it may be stored for reserve energy, (*c*) it may combine with other substances to form more complex compounds, e.g. lecithin.

Under normal conditions the ultimate fate of fat is its conversion into carbon dioxide and water. The first step in the process is the hydrolysis of the fat to fatty acids and glycerol. This is considered to be carried out by the enzyme lipase or esterase, which is found in practically all tissues of the body. The subsequent steps in the breakdown of the fatty acid molecule have been the subject of a number of theories. The isolation of intermediate products is difficult. It has been shown that in animals, which have been starved and then fed on a high fat diet (e.g. butter), substances known collectively as acetone bodies are found in the blood and urine. These acetone bodies, consisting chiefly of acetoacetic acid, β-hydroxy-butyric acid and acetone, are considered to be the end products in the oxidation of fat in the body. If some form of carbohydrate is fed with the fat, acetone bodies are not produced. This gives rise to the saying that "fat burns in the fire of carbohydrate, otherwise it smokes". In this case the carbohydrate is considered to be an antiketogenic substance.

Of the many theories advanced to explain the breakdown of fatty acids in the body, the one described by Knoop, and known as the β-oxidation theory, has received the most attention. According to this theory the long-chain fatty acids are oxidized at the β carbon atom (the second carbon atom from the carboxyl group) with the result that the two end carbon atoms are split off, oxidized to carbon dioxide and water through an intermediary hydroxy or keto acid, leaving a fatty acid containing two less carbon atoms. The oxidation process may then be repeated. Experimental work has shown that β-oxidation is undoubtedly the predominant reaction in the breakdown of fatty acids *in vivo*; however, other interpretations have been offered to explain certain phenomena. The presence of certain dicarboxylic acids in the urine after feeding C_8 to C_{11} fatty acids led Verkade (1936) to consider that ω-oxidation (oxidation on the terminal carbon atom) occurs simultaneously with β-oxidation. In this theory Verkade considers that oxidation of the terminal methyl group of the fatty acids gives rise to the

icarboxylic acids. The excretion of acetone bodies is usually greater after feeding he longer-chain fatty acids, e.g. palmitic and stearic, than after feeding the horter chain acids, e.g. butyric and caproic. In order to explain this finding,)euel *et al.* (1936) claim that a certain amount of δ-and ζ-oxidation occur along ʋith β-oxidation.

Since fatty-like material is an essential constituent of every cell in the body, ome of the ingested fat tends to be distributed throughout the whole body and s utilized in forming new cells. On the other hand, certain regions of the body ιppear to be used as fat storage depots, the most important places being the ·egion just under the skin, the superficial fascia, membranes surrounding the ɾidneys and intestines, and the intramuscular connective tissue. A very useful ɾechnique in following the fate of ingested fat is that worked out by Gage and ꟻish (1924), in which a fat is fed stained with the dye Sudan III. This dye com-ɔines with the fat and is not removed in the process of digestion. Such stained ɾat has been recovered from various depots of the body, in hen's eggs and in the milk of some species, but not in that of the cow.

The nature of the depot fat is quite markedly influenced by the nature of the fat fed. This is particularly evident in feeding hogs on fats of relatively low iodine value, whence a lard of low iodine value is obtained (Ellis and Isbell 1926). The iodine value of the milk fat can also be influenced by the degree of unsaturation of the ingested fat, according to Maynard *et al.* (1936). Under natural conditions the depot fat is quite characteristic of the species. This is quite evident for fish as explained in Section 2 of this Bulletin. Other factors besides dietary fat influencing the composition of the depot fat are environmental temperature, scale in evolution and, to a certain extent, selective deposition. The temperature of the environment tends to have an effect on the degree of unsaturation of the fat stored. This has been shown by Henriques and Hansen (1902) who kept a group of pigs at 0°C. and another at 35°C. The pigs at 0°C. deposited a fat of greater unsaturation than those at 35°C. This point is also illustrated in the fact that the outer layer of subcutaneous fat is more unsaturated and of lower melting point than the layers beneath (Hilditch 1935).

According to Eckstein (1929) there appears to be a selective deposition of fat. He found, in feeding one group of rats a diet containing a high percentage of sodium butyrate, and, another group triolein, that the butyrate radical was not deposited in the tissues while the triolein was. It was considered that the fatty acids of low molecular weight were utilized to synthesize saturated fatty acids of higher molecular weight.

The solution of the problem of fat breakdown for energy requirements is considerably hindered by the absence of adequate methods for isolating and determining intermediate compounds. Until methods are devised for studying this problem in more detail there must exist considerable doubt as to the normal mechanism of fat catabolism. It is not known how fats are utilized. Indirect evidence seems to favor a transformation of the fatty acid to carbohydrate. The glucose content of the blood of animals during hibernation does not decrease

materially nor are the glycogen stores depleted. On the other hand, the fat stores are decreased to a marked extent. The transformation of fat to carbohydrate has been followed in plant seeds. It has been shown that the fat content of cotyledons of the rape and other seeds during germination tends to decrease and the carbohydrate content to increase.

Fat is excreted mainly in the faeces, there being only traces in the secretions from the skin and practically none in the urine. Faecal fat is derived from a number of sources, unabsorbed fat of the diet, fatty material of bacteria, cellular material of the alimentary canal and possibly fat excreted from the wall of the large intestine. According to Sperry and Bloor (1924) the faecal fat is quite independent of the dietary fat. During fasting, fat amounts to one-third of the dry weight of the faeces and of this, one-third is unsaponifiable matter. Faecal fat differs in composition from food fat but resembles quite closely blood fat, and this fact has led some workers to believe that there is an excretion of fat into the large intestine. In the absence of bile the fat of the faeces is markedly increased. Shapiro et al. (1936) have studied the excretion of fat labelled with deuterium, and their results indicate that fatty acids are absorbed in the absence of bile, and at the same time fatty acids are excreted into the intestine and are not reabsorbed. On the exclusion of bile from the intestine it was found that the fatty acids of the faeces were equal to the intake, and yet 65 to 70 per cent of the labelled ingested fat was absorbed.

II. EFFECT OF DEGREE OF SATURATION OF DIETARY FAT

In the preceding Section it was pointed out that the nature of the depot fat, although quite characteristic of the species, could be influenced by the character of the food source. This factor is of considerable economic importance in the feeding of hogs since the degree of hardness of the pork is an important point in the market value of the product. In this connection advantage is taken of the change in unsaturation of the depot fat by modification of the diet. If the hogs are fed for a period on a diet containing unsaturated fat, and then the ration is changed for a short period to one containing considerably less unsaturated fat, the product obtained is harder and much firmer than if the hogs are fed continually on a diet containing considerable unsaturated fat. This change in the unsaturation of the body fat of animals is very well brought out in the work of Anderson and Mendel (1928). They have shown that the iodine value of the body fat of rats on a diet of various carbodydrates and proteins falls within the range of 55 to 70. These values tend to represent the degree of saturation of fat synthesized within the body from sources other than fat. Taking these values as a base line, they found that replacing 60 per cent of the energy intake with soya bean oil of iodine value 132 produced a body fat of iodine value 123; whereas feeding cocoanut oil of iodine value 8 produced a body fat of iodine value 35. These examples illustrate the marked influence of large intakes of fats differing widely in the degree of unsaturation, on the nature of the fat deposited. The influence of a number of fats including linseed oil, cod liver oil and olive oil upon

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the phospholipide and neutral fat of the body fat of the rat has been reported by Sinclair (1931). He states "there is a rough parallelism, but not a proportionality between the iodine number of the food fat and that of the neutral fat stored." It is generally recognized that the fatty acids present in the phosphatides of the body are of a higher degree of unsaturation than the fatty acids combined as glycerides in the depot fats. The degree of saturation of the former fatty acids is not subject to the influence of the dietary fat to the same extent as the fatty acids of the glycerides. On this account it is rather difficult to reduce the saturation of the fat of a tissue beyond a certain degree by feeding fat of a low iodine value. On the other hand, the degree of unsaturation of the fat of a tissue tends to be more proportional to the unsaturation of the dietary fat. It is also to be recalled, in using the iodine value of the fat extracted from a tissue as an index of saturation, that we are merely using a sort of weighted mean value of the separate iodine values of all its constituents.

The degree of unsaturation of the yolk fat of eggs can be markedly increased by feeding hens hempseed oil at a 28 per cent level of the ration, according to Cruickshank (1934). On the other hand the ingestion of a hard fat (mutton fat) at the same level did not significantly affect the degree of saturation of the yolk fat. This worker also found that the body fat of hens is markedly influenced by the dietary fat, irrespective of the degree of unsaturation. Owing to their higher metabolic rate the changes are more readily produced in them than in mammals.

The character of the food fat has a marked influence on the nature of the milk fat according to Maynard and co-workers (1936). They found that when a ration containing 3.5 per cent of fat with an iodine value of 107 was fed to cows, a milk fat was obtained with an iodine value of 38. When the fat component of the ration was changed to one of iodine value 43 a decided decrease in the iodine value of the milk fat to 26 occurred within three days. Hilditch and Thompson (1936) have obtained similar results in feeding rape seed, linseed or cod liver oil to cows. The results with cod liver oil are interesting in that it caused a reduction of the less saturated fatty acids of the milk fat to one half the normal content, while the proportion of oleic was much increased and there appeared 5 to 7 per cent of highly unsaturated C_{20} and C_{22} acids. There was no alteration in the proportion of polyethenoid C_{18} acids and there was no evidence that palmitoleic acid was appreciably absorbed from the oil. These workers suggest that the selective absorption of the highly unsaturated C_{20} and C_{22} acids of the cod liver oil by the enzymes responsible for the elaboration of typical milk fat retards their normal function, and causes the well recognized reduction in milk fat which follows the feeding of this oil to cows. It has been observed that the daily ingestion of 4 to 6 oz. of this oil causes as much as 30 per cent decrease in the milk fat. Similar results have been recently reported by Graham and Cupps (1938) following the daily feeding of 2 oz. of herring oil to goats. Similar amounts of the same oil after hydrogenation had little or no effect on the percentage of milk fat. These workers consider that the reduction of milk fat is due to a particular grouping of

unsaturated bonds in the fatty acids of the oil. The effect appeared to be generalized throughout the body rather than localized in the mammary glands.

III. ESSENTIAL FATTY ACIDS

It has been shown by Burr and co-workers (1929-1932) and Evans and co-workers (1928-1934) that young rats placed on a diet extremely low in fat manifest several characteristic abnormalities, namely a retardation in growth, a scaly condition of the skin and feet, an inflamed and often necrotic condition of the tail and the presence of blood in the urine. The administration of fats containing the unsaturated fatty acids linoleic (C_{18}) and linolenic (C_{18}) resulted in the resumption of growth and in a rapid disappearance of all signs of the so-called fatty-acid deficiency. No such beneficial effects followed the ingestion of the fat-soluble vitamins A, D or E, or of fats containing only the saturated fatty acids. Hence the above unsaturated fatty acids were termed essential fatty acids in that the body was unable to synthesize them from dietary foodstuffs.

Turpeinen (1938) has recently shown that arachidonic acid (C_{20}) should be added to the above list. He found it to be more effective than linoleic or linolenic acid in bringing about a cure of the fat deficiency symptoms. The important feature of the essential fatty acids, according to Turpeinen, is the presence of a double bond at the 9:10 and 12:13 positions of a fatty acid. The carboxyl group is not necessary since this may be changed to an alcohol group without destroying all the curative properties. Hume *et al.* (1938) claim that linolenic is less effective than linoleic in clearing up the skin symptoms, while docosahexaenoic acid (C_{22}) from cod liver oil increased the body weight of rats, but did not ameliorate the skin symptoms.

The isolation, identification and quantitative estimation of the above fatty acids in a fat or oil are difficult procedures. Moreover, the above dietary deficiency does not readily lend itself to a quantitative biological assay. On this account no definite statements can be made at present regarding the requirements of these essential fatty acids for mammals. It has recently been reported by Brown *et al.* (1938) that the adult human subject can exist for a period of six months on a very low fat diet without demonstrable harm. However, there was a marked decrease in the unsaturated fatty acids in the blood, and rats on the same diet exhibited the typical fatty-acid deficiency symptoms. This indicates that man, like the rat, is unable to synthesize the highly unsaturated fatty acids. Hansen (1934) has reported that the administration of the essential fatty acids, in the form of linseed oil, to eczematous children brought about an improvement in their condition. Boyd and Connell (1937) found a reduction in the incidence of colds among medical students after the administration of purified linoleic or linolenic acid (vitamin F).

The following oils are known to contain appreciable amounts of linoleic and linolenic acids and have been found to be very effective in bringing about a cure of the fat deficiency symptoms in rats: soya bean, linseed, cottonseed, corn, sesame and peanut. Thus far the fish oils have not been studied extensively as

curative agents in this deficiency disease. In referring to tables III, IV and V, Section 2, it will be seen that it is difficult to estimate accurately the amounts of linoleic and linolenic acids present in fish oils, because the results only show the total C_{18} acids, together with their average unsaturation. Green and Hilditch (1936), in a study of the C_{18} acids of cod liver oil, found about 70 per cent present as oleic and its isomers, about 10 per cent were tetraethenoid and the remaining 20 per cent contained no linolenic acid, and very little if any linoleic acid. In the case of the liver oil of the carp, evidence was obtained that, of the total C_{18} acids, 6 per cent was linoleic and 10 per cent linolenic. About 90 per cent of the C_{18} acids of whale oil was oleic and its isomers and about 3 per cent was tetraethenoid with small quantities of dienic acids. Lovern (1932) found the C_{18} acids of the liver oil of halibut to be exclusively monoethylenic and no linoleic could be detected.

These results lead one to believe that linoleic and linolenic acids are not present in fish liver oils in appreciable quantities. The fish body oils, however, have not received much attention in this respect and future work may show them to contain these essential fatty acids.

IV. ALLEGED TOXIC FACTOR OF FISH OILS

It has been reported by Agduhr (1926, 1934) that calves, pigs and most experimental animals develop rather serious and characteristic degenerative lesions of the heart and muscles when fed relatively large amounts (15 to 20 per cent of the diet) of cod liver oil for a period of several months. The factor responsible for these lesions was found associated with the saponifiable or glyceride fraction of the oil. This work has been confirmed by Madsen and co-workers (1935-1936) who have produced similar lesions in sheep and goats. According to McCay and co-workers (1935-1938) the same factor which produces the above lesions is involved in the reduction of the milk fat of cows when cod liver oil and other fish oils are fed at high levels. Norris and Church (1930) considered the toxic effects to be due to certain nitrogenous bases (isoamyline and choline) in the oils, but Bell and co-workers (1933) found no experimental basis for these conclusions. Yoshida (1937) reported similar toxic effects of shark liver oil in mice, and considered the effects to be due to the unsaturated fatty acids in the oil. He found that flavin obtained from yeast and liver was effective in preventing the toxicity. However, Burack and Zimmerman (1937) were unable to detect any beneficial effects of yeast on the toxicity of cod liver oil. Similar results were reported by McCay and co-workers (1938) who found that yeast did not counteract the lowering of the milk fat of cows. On the other hand, the toxic effects of cod liver oil were destroyed by hydrogenation. This suggests that certain unsaturated fatty acids in the fish oils are involved in the injurious effect obtained. It has been quite definitely shown that the toxic effects are not due to excess amounts of vitamin D or A in the oils, and vegetable oils do not exhibit the effect when fed at comparable levels.

It appears from the above results that fish oils contain a principle toxic

for farm animals and hence must be fed with a certain amount of discretion. On the other hand the beneficial effects obtained by feeding fish oils of good grade to farm animals at levels which contain prophylactic amounts of vitamins A and D are too well founded to cause undue concern regarding the injurious effects reported above.

V. EFFECT OF RANCIDITY

The factors influencing the rancidity of fats and oils have been adequately dealt with in Section 6 of this Bulletin. There remain to be discussed the effects on the animal organism of ingestion of rancid fats. The approach to a study of this problem is difficult on account of the objectionable odour and taste of rancid fats; most experimental animals refuse to consume quantities sufficient to make the results significant. This fact alone is possibly sufficient to lead one to believe that a toxic substance is present in rancid fats. In this connection Whipple (1932-1936) reports that a characteristic "oxidized fat syndrome", is produced in rats and dogs following the ingestion of rancid lard. On the other hand, Powick (1925) and Lease *et al.* (1938) report no harmful effects of the rancid fat itself, but a marked destruction of the vitamin A and carotene in the rancid fats and oils. The peroxides formed in a rancid fat are active oxidizing agents and these in turn act on vitamin A or its precursors in an oil, forming compounds which are no longer effective.

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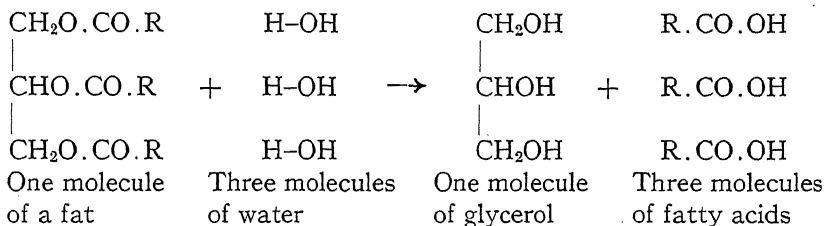DEUEL, J. H., L. F. HALLMAN, J. S. BUTTS AND S. MURRAY. *J. Biol. Chem.*, **116**, 621-639, 1936.

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SECTION 5. CHEMICAL AND PHYSICAL PROPERTIES OF FATS AND OILS

I. CHEMICAL PROPERTIES

(a) SAPONIFICATION

Fats (including fatty oils), as esters of fatty acids with the trihydroxy alcohol glycerol, have the property in common with other esters of breaking apart into their original constituents when acted upon by suitable reagents. This "splitting" of a fat into its constituent fatty acids and glycerol is an art dating back several centuries. It is represented by the accompanying equation in which R is the radical of *any* fatty acid.

$$
\begin{array}{ccccccc}
CH_2O.CO.R & & H\text{--}OH & & CH_2OH & & R.CO.OH \\
| & & & & | & & \\
CHO.CO.R & + & H\text{--}OH & \rightarrow & CHOH & + & R.CO.OH \\
| & & & & | & & \\
CH_2O.CO.R & & H\text{--}OH & & CH_2OH & & R.CO.OH \\
\end{array}
$$

| One molecule of a fat | Three molecules of water | One molecule of glycerol | Three molecules of fatty acids |

Actually, the splitting off of all three acid radicals probably does not take place simultaneously, but rather step by step, to give intermediate di- and mono-glycerides (see figure 1); but in the technology of marine animal oils the ultimate complete splitting is usually the aim. One hundred parts by weight of a typical fish body oil such as pilchard oil will theoretically yield about 95.5 parts of fatty acids and 10.5 parts of glycerol.

The foregoing equation represents a form of splitting known as *hydrolysis* since water is shown as the only reagent involved. The hydrolysis of a fat by water alone at ordinary temperatures is an extremely slow process. It may be hastened to a slight extent by the action of light, but much more so by the action of water at high temperatures in the form of steam under pressure. However, the high temperatures (140° to 200° C.; 280° to 390° F.) necessary for rapid hydrolysis with steam have a tendency to discolour the free fatty acids formed, and consequently various catalytic agents are used to accelerate the splitting at more moderate temperatures. The types of catalysts most frequently employed are: (1) acids, (2) enzymes, (3) complex organic compounds, (4) metallic oxides, (5) caustic alkalies. The exact mechanism of these catalytic reactions is very complex.

As stated above, the primary function of a fat-splitting catalyst is to hasten hydrolysis and to allow it to proceed at reasonable temperatures. The difficulty of hydrolysis of fats by water alone is partially due to the immiscibility of water and the liquid fat; as hydrolysis takes place only at the interfaces of the two

liquids, the reaction will proceed at relatively few centres unless violent agitation is effected, and this involves mechanical difficulties at the high temperatures and pressures necessary. A catalyst may merely hasten the hydrolysis at these interfaces without necessarily increasing the interfacial area or, what is more desirable, it may also enormously increase this area by the formation of emulsions of the water and oil during the early stages of the reaction. As the hydrolysis progresses, the fatty acids and glycerol formed tend to lessen the immiscibility of the oil and water. On a small scale, the same effect may be brought about by adding a third liquid (e.g. alcohol), in which both the oil and water can dissolve, thus greatly facilitating the hydrolytic action with or without the presence of a catalyst.

In all catalyzed reactions the catalyst promotes the synthesis of the original substance from its components as well as the breaking down of that substance into its components. In the particular case of catalyzed fat hydrolysis, there is therefore an equilibrium:

$$\text{Fat} \quad + \quad \text{Water} \quad \underset{}{\overset{\text{Catalyst}}{\rightleftharpoons}} \quad \text{Glycerol} \quad + \quad \text{Fatty acids}$$
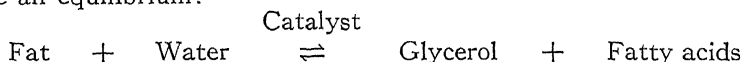
which prevents the hydrolysis from being complete. An excess of *reacting* water, or removal of the glycerol or fatty acids (or both) as fast as they are formed, will shift that equilibrium towards the right and tend to cause hydrolysis of the fat to proceed to completion. In practice, it has been found most convenient to render the fatty acids non-reactive as they are produced, by neutralizing them with an alkali to form soaps. The alkali is added to the original fat, and performs the functions of both a catalyst and a remover of the fatty acids. This particular type of hydrolysis is called *saponification*, a term that is frequently employed to denote the splitting of fats whether soaps are actually formed or not. If soaps are not the end product desired, the fatty acids may be recovered by treating the soaps with a mineral acid.

A very brief synopsis of the characteristic form of hydrolysis brought about by each of the five previously-mentioned types of catalysts used in fat splitting is presented under the headings which follow; the technical applications are described in Section 8 II (a).

(i) ACID HYDROLYSIS

Dilute mineral acids such as hydrochloric and sulphuric have a decidedly accelerating effect on fat hydrolysis at elevated temperatures, but there are practical difficulties in maintaining a sufficiently large interface between the acidulated water and the oil. Moreover, the hydrolysis tends to slow up towards the end of the process and it never proceeds to completion. Nitric acid is prone to cause oxidation and possible elaidinization [this Section, I (j)] of the fatty acids. Concentrated sulphuric acid is employed in many instances, as it has an original emulsifying action on the oil; with saturated fats, it acts purely as a catalyst, but with unsaturated fats a certain amount of sulphation [this Section, I (f)] takes place, these sulphated products further assisting in the emulsification. The fatty acids eventually produced are usually very dark.

(ii) ENZYMATIC HYDROLYSIS

Enzymes are complex organic chemical compounds found in plant and animal tissues, and act as catalysts in vital processes. The particular enzymes that promote the hydrolysis of fats are known as *lipases*, and are found principally in seeds (especially the castor bean) and in the digestive organs and liver of animals. They hydrolyze fats at ordinary temperatures in the presence of moisture (preferably a water-in-oil emulsion), but exert optimal catalytic activities at temperatures varying from 20° to 30° C. (68° to 86° F.) depending on their nature. They are all rendered inactive at 100° C. (212° F.).

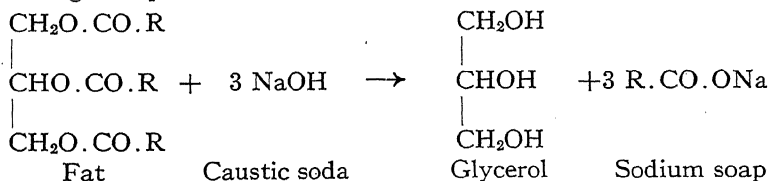(iii) HYDROLYSIS BY SYNTHETIC ORGANIC CATALYSTS

Twitchell (1900) prepared a very suitable catalyst by heating 10 parts of oleic acid with 3 parts of naphthalene to 50° C., then treating the mixture with 30 parts of concentrated sulphuric acid. The resultant product was washed free of acid and dried, and probably had the constitution of a sulphonaphthalene stearic acid. Later investigators have prepared similar sulphonated compounds, using aromatic substances other than naphthalene, other fatty acids and hydrogenated castor oil. Some contain no fatty material. Many are patented and sold under trade names (e.g. Pfeilring, Kontakt, Idrapid, Nekal BX). The amount of catalyst used varies from 0.5 to 1 per cent of the weight of the oil; the action is essentially a combination of emulsification and hydrolysis by the sulphonic acid radical.

(iv) SAPONIFICATION WITH METALLIC OXIDES

Calcium oxide (lime) and the oxides of magnesium, zinc and lead all exert a catalytic action in the hydrolysis of fats, and combine with fatty acids to form the corresponding water-insoluble metal soaps. These oxides may be added to the extent of 3 to 4 per cent of the weight of the fat in the hydrolysis of fats by steam under pressure by means of the autoclave process, in which case they exert a strictly catalytic action in addition to their saponifying action. The soaps formed are soluble in the remaining oil and promote the hydrolysis by allowing the formation of water-in-oil emulsions. In the lime saponification process of soap making, sufficient lime in the form of a thin paste with water is employed to combine with *all* the fatty acids liberated and this is thus a true saponification process.

(v) SAPONIFICATION WITH CAUSTIC ALKALIES

Saponification of fats by caustic soda or caustic potash is a very old process, and is used to a great extent technically because of the fact that the ordinary soaps of commerce result from the neutralization of the fatty acids by the alkali during the process.

$$
\begin{array}{c}
CH_2O.CO.R \\
|\\
CHO.CO.R \quad + \quad 3\ NaOH \quad \rightarrow \\
|\\
CH_2O.CO.R \\
\text{Fat} \qquad \text{Caustic soda}
\end{array}
\qquad
\begin{array}{c}
CH_2OH \\
|\\
CHOH \qquad +3\ R.CO.ONa \\
|\\
CH_2OH \\
\text{Glycerol} \qquad \text{Sodium soap}
\end{array}
$$

or a given fatty acid, the soap formed from caustic potash is softer than that om caustic soda. Complete hydrolysis of a fat may be brought about by less lkali than is necessary to combine with the fatty acids formed, but the tempera- re must be high; so it is customary to use a concentrated alkali to permit omplete saponification within a reasonable time at lower temperatures. The cceleration of the reaction is due to the emulsifying action of the soap first ormed, and, since heat is generated during the saponification, this heat may e utilized to the exclusion of added heat if the emulsification is maintained 1echanically. Saponification may be made a continuous process (British patent 23,188) by passing the aqueous alkali and oil through a tube heated to a tem- erature of 280° to 300° C., the duration of exposure to the heat being only ome 30 seconds. A recent review of the mechanism of saponification of fats y alkalies has been given by Lascaray (1939).

Numerous other variations of fat-splitting processes are known, including aboratory methods designed for rapid determination of the saponification value nd unsaponifiable content as criteria of fats and fatty oils.

An electrolytic action in conjunction with a Twitchell reagent has been laimed (American patent 1,976,376) to reduce the time of technical hydrolysis rom 24-36 hours to about 8 hours.

The hydrolysis of fatty compounds other than fats is briefly described in the introduction to Section 3. III (d) of that Section mentions the difficulty of saponifying waxes, due in part to the circumstance that the fatty alcohol, unlike the glycerol from fats, is insoluble in aqueous reagents. The use of very con- trated alkali at high temperatures partially saponifies waxes, but it is more efficient to employ an alcoholic solution of the alkali.

(b) HYDROGENATION

The liquid glycerides of fish oils contain a high proportion of unsaturated fatty acids, while in the solid glycerides saturated fatty acids predominate. The presence of highly unsaturated acids renders the fat or oil susceptible to oxidation and consequent rancidity, thus making it undesirable in this form for use in soap, margarine and other industries.

The only difference between the unsaturated and saturated fatty acids which confers the higher melting points on the glycerides is the smaller pro- portion of hydrogen in the former. Accordingly, if hydrogen could be added to the unsaturated fatty acids it should be possible to convert them into saturated acids.

(i) PREPARATION OF CATALYSTS

Although unsaturated acids undergo addition reactions, it is not possible to make hydrogen add directly at the double bond merely by bringing the oil into intimate contact with hydrogen. However, if a small amount of a metal such as nickel, platinum or palladium, prepared in a special manner, is introduced into the oil, it is possible to cause hydrogen to add at the points of unsaturation with resultant hardening of the oil.

Platinum and palladium are used mainly in laboratories because of their relatively greater activity and the lower temperature of reaction, but on account of the expense it is not feasible to employ these metals for the industrial hydrogenation of oils. Platinum catalysts may be prepared by the fusion of platinum chloride with sodium nitrate according to Adams' method, producing platinum oxide which is reduced in the reaction mixture by means of hydrogen (Vorhees and Adams 1922; Adams and Shriner 1923). The preparation of palladium catalysts may be accomplished in a similar way.

Platinum or palladium chloride solutions may also be reduced by formaldehyde (Loew 1890) or phenylhydrazine (Kaffer 1924) with or without a support such as carbon, and the precipitated mass filtered, dried and introduced into the reaction mixture.

Nickel is used commercially since it is inexpensive, readily prepared in a highly active condition and is generally a robust catalyst. Its preparation may be accomplished in numerous ways which may be classified as follows:

A. The catalyst may be prepared separately and introduced into the substrate

(a) without support. (1) Nickel nitrate is calcined to the oxide and reduced in hydrogen; or (2) nickel hydroxide or carbonate is precipitated from a soluble salt, washed thoroughly, dried and reduced in hydrogen,

(b) utilizing an inert support such as kieselguhr. (1) Nickel hydroxide or carbonate is precipitated in the presence of the support, the mass filtered, thoroughly washed, dried and reduced in hydrogen; or (2) the nickel salt is precipated separately and, after washing, suspended with the support, filtered, dried and reduced in hydrogen.

(c) in massive self-supporting form. (1) The surface of nickel turnings or gauze is etched by acid or anodic oxidation; or (2) nickel aluminium alloy is treated with sodium hydroxide to dissolve part of the aluminium, leaving a porous surface of nickel.

B. The catalyst is produced in the body of the substrate by the reduction of nickel acetate or formate.

Numerous salts of nickel have been used in the preparation of these catalysts; the nitrate free from arsenic, chlorides and sulphur is a common source for use either in direct calcination or in the precipitation methods with or without a support. Nickel sulphate has been shown to be a satisfactory source of nickel (Ellis, 1930, p. 121) and nickel acetate and formate may be used directly and reduced in the presence of the substrate. Many other salts such as the borate, silicate, etc., may be used in various ways, but they have not found general use.

The direct calcination of the nitrate in air produces an oxide which is resistant to reduction and only two-thirds of the material can be reduced at 420°C. (Senderens and Aboulenc 1912). However, the catalyst thus prepared is active. Active catalysts may be prepared by reducing at temperatures as low as 300°C. (Gauger and Taylor 1923). By precipitating the nickel as the hydroxide or carbonate followed by thorough washing to remove all traces of alkali, a material is obtained that is much less resistant to reduction than the oxide prepared by calcination of the nitrate. Iki (1928) prepared the oxide by anodic oxidation of nickel in the presence of alcohol which rendered the oxide non-adherent to the metal electrode. The oxide is thus obtained free from sulphate which it is claimed persists in the carbonate precipitation method. However, it has been shown that the presence of traces of sulphate are harmless and that nickel oxide may be prepared satisfactorily from this salt (Ellis 1930, p. 121).

The commercial methods of reducing catalysts are essentially the same as those of the laboratory, i.e. (1) straight reduction in hydrogen, (2) reduction in two stages at 200 to 300°C., first at 1 atmosphere of hydrogen, and second at 4 to 5 atmospheres of hydrogen, (3) surface reduction, or (4) reduction in a liquid medium, such as paraffin wax, vaseline, melted fat, naphthalene, etc.

The wet method of reduction, that is reduction in a liquid medium, requires a lower temperature than reduction of the dry catalyst. The temperature at which nickel oxide can be reduced depends on the method of preparation and the treatment prior to reduction. In general, reduction at red heat produces an inactive catalyst, probably due to sintering and the consequent lessening

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ι the amount of active surface. Reduction of the dry oxide is not complete below 300°C., but very active catalyst is obtained which must be used immediately. The optimum temperature)r activity and ruggedness appears to be somewhere about 350°C. Catalysts prepared by dry ɔduction are usually pyrophoric, but this character is no criterion of activity as a hydrogenation ɔatalyst (Armstrong and Hilditch 1921). Incompletely reduced oxides are more active than hose which are completely reduced, probably because of the higher temperature required for ɔomplete reduction (Armstrong and Hilditch 1921).

When the catalyst is reduced apart from the substrate, it must be cooled in an inert atmos-,here such as carbon dioxide or hydrogen in order to prevent re-oxidation upon contact of the .ot metal with oxygen of the air. It is preferable that the transfer of the catalyst from the ɔeduction and cooling vessel to the hydrogenation chamber be carried out in an inert atmosphere.

The precipitation of nickel may be as the hydroxide, carbonate or the bicarbonate, but horough washing of the precipitate is a most important process. An unwashed precipitate of ɩickel bicarbonate showed no activity as a hydrogenating catalyst, so Normann (1936) prepared he bicarbonate separately and thoroughly washed it before suspending it with kieselguhr to ɔecure a supported catalyst, because he found it difficult to wash the mass thoroughly when)recipitated in the presence of the support. It appears that the complete removal of the excess ιlkali is essential for obtaining an active catalyst. A catalyst which in aqueous suspension ;ave a distinctly alkaline reaction to phenolphthalein was not nearly as active as the same one ιfter washing until it showed no reaction with the same indicator (Riddell, unpublished data). Γhe pH of the catalyst may have a distinct bearing on the activity.

It is apparent from the literature and from work in these laboratories that the support ιas an important bearing on the activity of the catalyst, probably due to the presence of small ιmounts of elements that exert either a promoting or an antagonistic action on the active metal. Furthermore, the relative acidity or basicity of the support may be an important factor though :here is considerable difference of opinion as to the actual effect. The main purpose of the ɔupport is to increase the surface exposed and thus the capacity for adsorbing hydrogen; also the support makes the catalyst less easily inactivated by too high temperatures during reduction, ɛ.g. an unsupported catalyst that was seriously impaired in its action when reduced at 500°C. ɔtood 40 minutes at that temperature when on a support without noticeable damage (Ellis 1930, p. 118). Usually the supported catalyst is not reduced below 350°C. and the optimum is between 350° and 500°C. (Armstrong and Hilditch 1921; Kelber 1916; Taylor and Burns 1921).

A process that appears to be gaining favour is the wet reduction method. That is, the catalyst is reduced in the oil to be hydrogenated at temperatures somewhat above the normal temperature for hardening the oil. Because of some decomposition of the oil at these temperatures it is usual to carry out the reduction of the catalyst in a small portion of the oil, or in some other non-injurious medium, in order to prevent subjecting the whole mass to the more elevated temperatures. In certain cases where the product is required for edible purposes the nickel is filtered out of the oil after reduction and washed with fresh oil in order to eliminate a "scorched" taste that otherwise would be present.

The main advantage of the wet reduction method is the convenience in dispensing with the necessity of cooling and transferring the dry catalyst in an inert atmosphere from the reduction chamber to the mass of oil. It is usual to use the formate and occasionally the acetate in the preparation of this catalyst. During the reduction of the catalyst the oil is almost completely hydrogenated and assumes a relatively high melting point; consequently it is possible to prepare a batch of catalyst and use it as required by cutting the desired quantity from the mass.

Another form of catalyst is prepared by the action of sodium hydroxide on a nickel-aluminium alloy containing approximately 50 per cent aluminium. The lighter metal may be dissolved completely, leaving a porous form of nickel with a large surface which is very active catalytically (Raney 1927). If desired, only part of the aluminium metal may be dissolved, leaving a massive self-supporting catalyst with a porous surface. This type of catalyst is reported to be insensitive to the usual poisons and particularly suitable for hardening fish oils.

Another type of massive catalyst is that used in the Technical Research Works (T.R.W.) continuous process. As originally designed, the catalyst consisted of a cylindrical gauze container filled with nickel turnings. The latest type of catalyst consists of pure nickel elements constructed in such a way as to eliminate the surrounding cage. The catalysts are made the anode in a dilute solution of sodium carbonate and oxidized electrolytically at low current densities. The thin film of oxide which is produced on the surface of the metal is reduced in the hydrogenating plant with hydrogen at elevated temperatures, after which it is ready for use in the hardening process (Bolton 1927; Lush 1927).

(ii) MIXED CATALYSTS

Frequently nickel catalysts are prepared with the addition of varying amounts of other metals such as copper and chromium. These added metals act as promoters, auxiliary- or co-catalysts.

These mixed catalysts frequently permit reduction at lower temperatures than nickel oxide alone, copper-nickel catalyst on a support being reduced at 180° C., while nickel oxide alone is reduced at 300° C. or higher (Armstrong and Hilditch 1922).

Mixed catalysts are frequently used in high-pressure hydrogenation and it is possible that the promoter has a directive effect on the reaction. It has been shown by Adkins (1937) that copper-chromium oxide catalyst is less selective in its action toward the carboxyl group than a zinc-chromium catalyst, and that a properly chosen catalyst may markedly influence the course of the reaction in high-pressure hydrogenation.

The usual method of preparation is to co-precipitate the catalyst and its associated metal by sodium carbonate or hydroxide from a solution in which is suspended the desired support. Mixtures of nickel and copper formate may be reduced in oil, using the wet reduction method to give satisfactory results.

(iii) TEMPERATURE

Usually hydrogenation with platinum or palladium catalysts is carried out at room temperatures or very slightly elevated temperatures, but the usual procedure with nickel catalysts is to carry out the reaction at temperatures between 175° and 225° C. Until recently it was considered that hydrogenation with nickel catalysts would not proceed at an appreciable rate using ordinary pressures, unless temperatures upward of 120° were used. However it has been shown that with colloidal nickel (Waterman, van Vlodrop and Pezy 1936) and

e Raney catalyst (Dupont 1936), hydrogenations can be carried out at room mperature or very slightly above. The advantage claimed for these methods that there is no extensive destruction of the vitamin A contained in the oil.

The effect of increasing the working temperatures is to increase the selecivity of hydrogenation, that is, the more highly unsaturated acids in the glyrides are reduced stepwise to the less highly unsaturated before any saturated ids are formed. As the temperature is raised, a critical value is reached where ie formation of "iso"-acids (solid unsaturated acids) begins to take place. At mperatures above this value, which may vary from oil to oil, the hydrogenated roduct has a higher melting point for a given iodine value than an oil hydronated at lower temperatures. The increase in selectivity of hydrogenation is nderstandable when it is considered that the optimum hydrogenation temperture of oleic acid is 170°C., while the rate of hydrogen uptake for linolic acid icreases steadily to 250°C. Thus, in an animal oil such as pilchard oil in which ie glycerides are made up of complex mixtures of acids (Brocklesby and Harding 938), if the lower unsaturated acids have a lower optimum temperature for eaction than the higher unsaturated, raising the temperature will cause the latter ɔ be hydrogenated first.

(iv) PRESSURE

In the absence of interfering factors the rate of absorption of hydrogen is ɔroportional to the pressure. However, the presence of impurities in the oil vhich gradually poison the catalyst, and the accumulation of impurities in the ɡaseous phase are obvious disturbing factors. Others that may disturb the proɔortional absorption are the possible selective adsorption of the gaseous impuri-ɔies on the surface of the catalyst, and the presence of groups in the molecule that might be selectively adsorbed on the surface of the catalyst but not reducible.

The reaction rate at 180°C. and 360, 760 and 1160 mm. pressure of hydrogen, using nickel on kieselguhr with olive oil, oleic acid and ethyl oleate, is approximately of the first order, but at higher pressures the rate is more rapid than one of a first order. The constants are independent of the number of double bonds in the molecule (Kailan and Kohberger 1932).

When hydrogenation is carried out at higher pressures there is a tendency to cause the formation of saturated fatty acids before the complete selective hydrogenation of the more unsaturated acids has taken place (Waterman, van Tussenbroek and van Dijk 1931). Selective hydrogenation is obtained at low pressures and high temperatures. It requires less hydrogen to produce a product of given melting point at high pressures than at low, due to the earlier, more rapid formation of saturated fatty acids.

(v) AMOUNT OF CATALYST

The quantity of catalyst used in the hydrogenation of oils has an appreciable bearing on the course of the reaction. The weight of evidence seems to be that increasing the amount of catalyst increases the selectivity; Dhingra, Hilditch and Rhead 1932; Richardson, Knuth and Milligan 1924; and see also, Ubbelohde

and Schönfeld 1931; Etinburg, Stelin and Krushevski 1935).   The increased amount of catalyst also increases the formation of iso-acids.

(vi) HIGH PRESSURE HYDROGENATION

Fats, fatty acids and their esters may be reduced to the corresponding alcohols under high pressures of hydrogen in the presence of suitable catalysts (Adkins 1937).   The usual catalyst for this type of reduction is either a combination of copper oxide and chromium oxide (copper chromite) sometimes promoted by the addition of calcium, barium or iron, or the usual nickel catalyst promoted by copper.

Adkins' catalyst was prepared from precipitated copper ammonium chromate by careful heating to give a voluminous powder that was an active hydrogenation catalyst (Adkins and Connor 1931; Connor *et al.* 1932).   Reduction of fatty acids to alcohols can be accomplished at about 220 atmospheres pressure and 250°C. (Adkins and Folkers 1931).   This is a type of reduction similar to the sodium-alcohol method of Bouveault-Blanc.

A recent patent describes a high-pressure continuous system (B.P. 433,549, 1934) where the fatty acids are mixed with a barium-copper chromite catalyst using vigorous agitation by hydrogen in the reaction chamber, at 5-40 atmospheres pressure and a temperature of 260° to 300°C.   The alcohols are carried off in the hydrogen stream to a condenser.

(vii) CONJUGATED HYDROGENATION

It has been shown that simultaneous hydrogenation and dehydrogenation may occur in the presence of catalysts.   When oleic acid and ethyl alcohol are heated together in the presence of nickel, stearic acid and acetaldehyde are obtained.   This process has received considerable attention from Russian workers and may become of some importance technically (Lyubarskii 1932; V. Puzanov and Ivanova 1935).

(viii) CATALYST POISONS

It is necessary to purify both the hydrogen and fat before undertaking hydrogenation.   Slight impurities in the gaseous phase collect and increase in

TABLE XVII.   Influence of small amounts of impurities on rate of hydrogenation of pilchard oil

Substance added	Active constituent	Concentration (%)	Decrease in rate of hydrogenation (%)
Cystine	Organic sulphur.........	0.001	75
Glycine	Organic nitrogen........	0.10	50
Lecithin	Organic phosphorus......	1.0	95
Oxidized oil	Organic peroxides.......	1.8	17
Water soluble nitrogenous matter from decaying fish flesh	Amines................	0.02	67

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oncentration, and many have a specific inactivating action on the catalysts. Free fatty acids, phosphatides or mucilaginous substances in the oil also act as poisons, and should be removed by suitable refining processes followed by drying the oil, as water vapour is an active catalyst poison. Arsenic, sulphur, phosphorus and lead compounds and carbon monoxide are active catalyst poisons. In some experiments made in these laboratories (Charnley, unpub.) small quantities of impurities which might possibly be found in low-grade fish oils were added to samples of a refined pilchard oil. These were then hydrogenated with the results shown in table XVII.

(ix) HYDROGENATION OF FATS AND OILS

In the many investigations that have been carried out on the hydrogenation of oils and fats, it has been well established that when nickel catalyst is used at
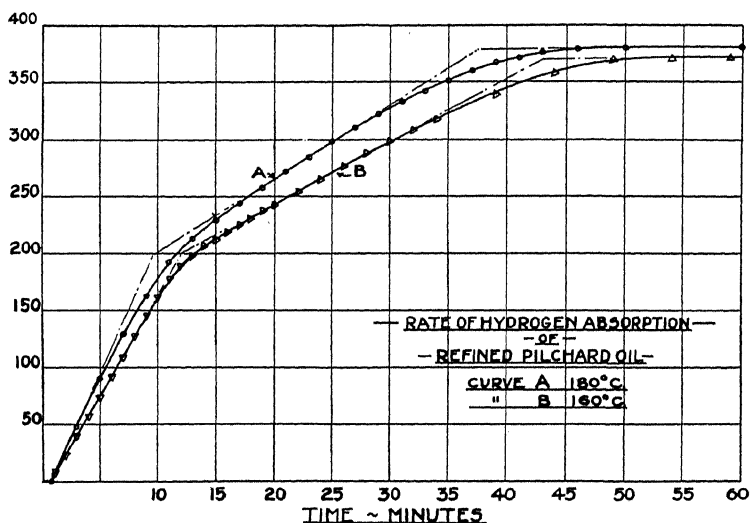
FIGURE 9.

ordinary pressures of hydrogen and elevated temperatures, the process is selective and proceeds essentially in a step-wise manner.

In the hydrogenation of pilchard oil, Brocklesby and Charnley (1933) have shown that the rate curve for hydrogenation bears a general resemblance to the unimolecular type and is really made up of a series of linear sections. This corresponds to the results of Armstrong and Hilditch (1920) using pure compounds. The results for pilchard oil are shown in figure 9 for hydrogenation temperatures of 160° and 180°C. using 1 per cent nickel-to-oil and atmospheric pressure of hydrogen. During the reaction it was shown that there was practically no increase in saturated acids until after the complete disappearance of the highly unsaturated acids as indicated by the octo- and hexa-bromide tests.

Recent detailed studies by Hilditch *et al.* on the changes occurring in the

composition of known glycerides have given further insight into the course of hydrogenation. It was considered that there might be a difference in the rate or the susceptibility to hydrogenation of the α- and the β-mono-unsaturated disaturated glycerides (Hilditch and Jones 1932), but more recent work has shown that any apparent difference was due to the varying ratios of the glycerides under investigation (Bushell and Hilditch 1937). It has been conclusively shown as a result of this work that with oleo-glycerides all the unsaturated components are reduced concurrently but that the tri-oleo compounds are reduced more rapidly than the di-oleo and these in turn more rapidly than the mono-oleo glycerides.

Thus, in the hydrogenation of natural fats made up of glycerides containing saturated, mono-, di- and poly-unsaturated fatty acids, it appears that the rate of hydrogenation of the highly unsaturated acids is sufficiently rapid to go practically completely to the lower stages of unsaturation before any appreciable amount of hydrogenation of the mono-unsaturated acids occurs. When this stage is reached we have the conditions outlined above, with all unsaturated components being reduced simultaneously but at different rates for the tri-, di- and mono-unsaturated glycerides.

In the high pressure hydrogenation of fats and oils the ester group of the glycerides is attacked with the formation of the corresponding alcohols. This process usually results in the saturation of any double bonds as well, but may be carried out in a selective manner to produce unsaturated alcohols. For example, butyl oleate hydrogenated over zinc-chromium oxide catalyst at 280° to 300°C. for 11 hours at 100 atmospheres pressure, gives 63 to 65 per cent octadecenol (Sauer and Adkins 1937).

The effect of hydrogenation on the naturally occurring pigments, sterols and vitamins is in general to bring about their complete reduction. The multiple double bond system is reduced in ordinary catalytic reductions, with loss of the characteristic colour of the pigment and the destruction of the vitamins present. However, if the process is carried out at low temperatures, e.g. 50°C., using colloidal nickel as the catalyst (Waterman et al. 1936) a considerable hardening may be secured with little loss of colour or vitamin activity. The hydrogenation under these conditions is selective and the product obtained may be used in margarine.

(x) HYDROGENATION OF POLYMERIZED OILS

As a result of the reduction in the number of active double bonds during polymerization, there has been a number of investigations into the hydrogenation of polymerized oils for such purposes as soap stock.

The work of Dittmer (1927), Bag (1929) and Kino (1931) showed no conclusive evidence that there was, or was not, depolymerization during hydrogenation of the polymerized oils. A series of experiments was carried out (Brocklesby and Riddell, unpub. data) using cottonseed oil and pilchard oil polymerized to various degrees, the former at 290°C. and the latter at 250°C. for times up to twenty-four hours. These were hydrogenated over nickel on infus-

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ial earth at 180°C. and the rate of hydrogenation determined as well as the tal hydrogen uptake. In figure 10 are shown the curves for hydrogenation polymerized pilchard oil and it is seen that the rate of hydrogenation and the tal uptake of hydrogen decrease as the degree of polymerization increases. his corresponds to the disappearance of the highly unsaturated acids during lymerization. Brocklesby and Denstedt (1934) showed that when pilchard oil as polymerized at 250°C., the highly unsaturated acids had completely disap- ared in six hours. It is also clear that there is no evidence of depolymerization continued hydrogenation. In several instances this was continued for several urs after absorption had apparently ceased and no further hydrogen was sorbed.
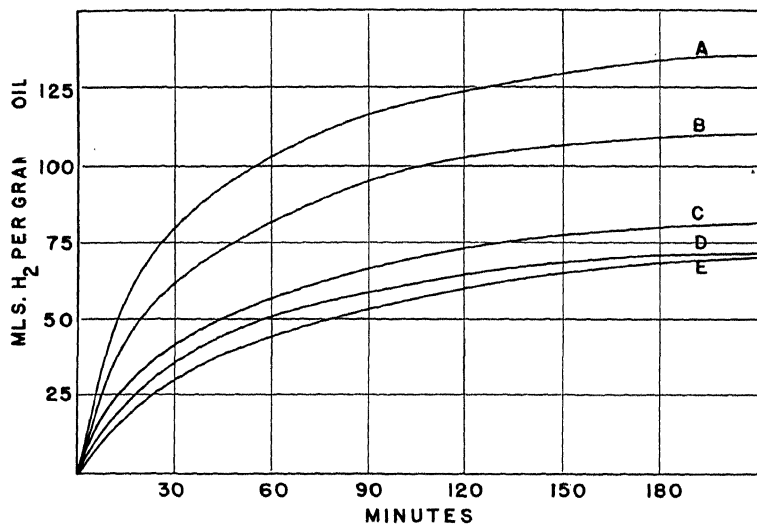
FIGURE 10. Hydrogenation of polymerized pilchard oil. A, unpolymerized oil; B, polymerized 4 hours at 250°C.; C, polymerized 12 hours at 250°C.; D, polymerized 16 hours at 250°C.; E, polymerized 24 hours at 250°C.

In order to give further proof of this point, a sample of highly polymerized cottonseed oil was saponified and re-esterified with methyl alcohol. The un-polymerized esters were distilled off in a Hickmann still and the polymer remain-ing was subjected to hydrogenation under the above conditions. It was found that no hydrogen was absorbed, thus showing that there was no depolymerization during hydrogenation over nickel at ordinary pressures of hydrogen at 180°C.

Neither the introduction of fresh portions of catalyst at any stage of hydro-genation, nor alkali-refining the polymerized oil caused any appreciable change in the rate of hydrogenation, which showed that the decreasing rate and total hydrogen absorption were not due to increasing amounts of poison in the poly-merized samples.

(c) OXIDATION.

In a previous section it has been shown that substances containing unsaturated bonds become saturated by the addition of hydrogen, halogens, oxygen, etc. The iodine value is used as a measure of the degree of unsaturation and table XVIII shows the range in the iodine value for a number of typical oils. The first six oils listed have low iodine values and do not react readily with oxygen of the air, hence are known as non-drying oils, or oils which do not oxidize to form a film. The next few oils in the list react slowly with oxygen and are known as semi-drying oils, while linseed, chinawood and pilchard oils with high iodine values are classed as drying oils, as they oxidize readily to form tough, elastic films when exposed to the air. The oils which oxidize in this way have extensive application in the paint and varnish industry.

TABLE XVIII. Unsaturation of oils as shown by iodine values.

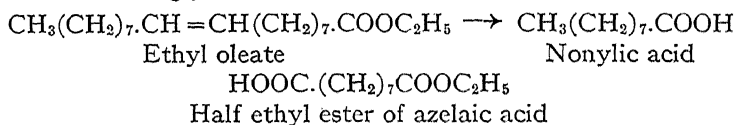| Fat or oil	Iodine value, range
Coconut oil	7– 11
Cacao butter	32– 41
Mutton tallow	35– 46
Beef tallow	38– 46
Lard	46– 70
Olive oil	79– 88
Peanut oil	83–100
Corn oil	111–130
Shark liver, grayfish liver, etc.	110–135
Soya bean oil	119–135
Whale oil	121–146
Seal oil	127–141
Salmon body oil	125–165
Herring oil	123–142
Menhaden oil	139–173
Chinawood oil	160–180
Pilchard oil	176–186
Linseed oil	173–185

The activity of these oils with respect to oxygen is a function not only of the number of double bonds present in the component fatty acids, but of the position of the double bond in the molecule. Thus, the closer the bond is to the carboxyl group, the less readily is oxygen absorbed and the more acidic is the peroxide that is formed by the absorption of oxygen. In fatty acids containing a system of multiple double bonds there will be a difference in the rate at which the individual double bonds react, particularly when they form a conjugated system.

These oils are oxidized by other reagents as well as oxygen, potassium permanganate, peracids, peroxides and ozone all bringing about oxidation.

Aqueous potassium permanganate brings about the addition of hydroxyl oups to the double bond according to the following scheme:
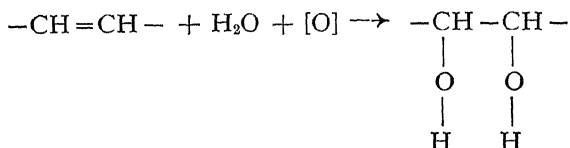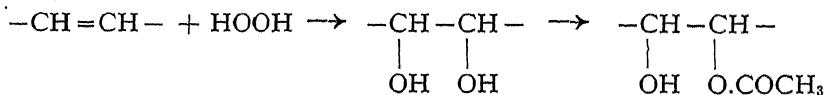
$$-CH=CH- \; + \; H_2O \; + \; [O] \longrightarrow \; \underset{\underset{H}{\overset{|}{O}}}{\overset{|}{-CH}} - \underset{\underset{H}{\overset{|}{O}}}{\overset{|}{CH}} -$$

owever, the reaction usually causes the formation of acids by the further cidation of the carbon atoms bearing the hydroxyl groups. Thus oleic acid ves 60 per cent dioxy stearic acid, 16 per cent azelaic acid and 16 per cent oxalic :id along with a small amount of nonylic acid when the oxidation is carried out : 60°C. In non-aqueous solutions, such as acetone or glacial acetic acid, quantative oxidation of the double bonds is obtained with the formation of the ιono- and dibasic acids or their half esters (Armstrong and Hilditch 1925), and ιere is no formation of the hydroxy compounds, the process resembling the action f ozone more than that of the aqueous permanganate. Since this reaction can e controlled more easily in acetone than in an aqueous medium due to the reater solubility of the oils in the former solvent, it is used as the reaction ιedium for the oxidation of unsaturated acids and glycerides in determining aturated acids and glycerides.

$$CH_3(CH_2)_7.CH=CH(CH_2)_7.COOC_2H_5 \longrightarrow CH_3(CH_2)_7.COOH$$

Ethyl oleate　　　　　　　　　　　　Nonylic acid

$$HOOC.(CH_2)_7COOC_2H_5$$
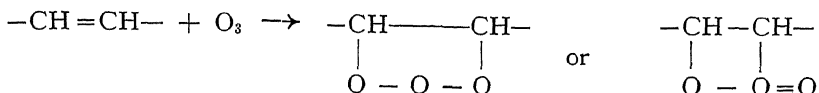
Half ethyl ester of azelaic acid

Peracids bring about hydroxylation of the double bond with little splitting ιf the carbon chain in the simpler unsaturated systems such as oleic acid, but the eaction may not be so clear-cut in the poly-unsaturated compounds.

Peroxides, particularly hydrogen peroxide, have a preliminary hydroxylating :ffect followed by a complex attack upon the carbon chain, which is catalysed ιy the presence of copper. In a non-aqueous medium such as tertiary butyl ιlcohol and in the presence of such catalysts as vanadium, chromium or molybdenum oxides the reaction stops at the hydroxylated stage. In acetic acid solution ιf hydrogen peroxide, peracetic acid is formed and with short chain fatty acids there is oxidation of the α-carbon atom and probably some β-oxidation as well. However, the longer chain acids are less susceptible to this type of reagent, while with the long chain unsaturated acids the reaction stops after hydroxylation and acetylation of the hydroxyl groups, the latter process being more complete at higher temperatures.

$$-CH=CH- \; + \; HOOH \longrightarrow \; \underset{\underset{OH}{\overset{|}{}}}{\overset{|}{-CH}} - \underset{\underset{OH}{\overset{|}{}}}{\overset{|}{CH}} - \longrightarrow \; \underset{\underset{OH}{\overset{|}{}}}{\overset{|}{-CH}} - \underset{\underset{O.COCH_3}{\overset{|}{}}}{\overset{|}{CH}} -$$
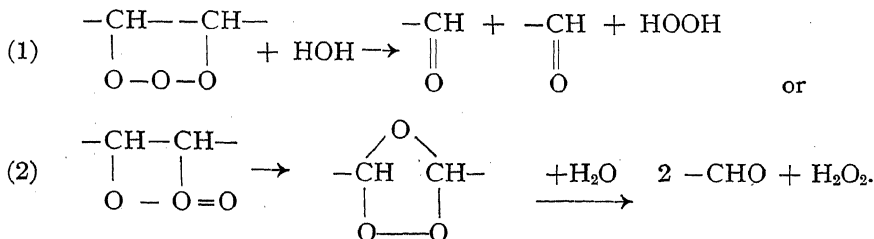
Ozone is an active reagent in the presence of unsaturated bonds, forming solid addition products when the reaction is carried out in non-aqueous, inert

media. These addition products are known as ozonides and in some cases are highly explosive. They may be represented by the following scheme:

$$-CH=CH- + O_3 \longrightarrow \begin{matrix} -CH\text{------}CH- \\ | \qquad\quad | \\ O-O-O \end{matrix} \quad \text{or} \quad \begin{matrix} -CH-CH- \\ | \qquad | \\ O-O=O \end{matrix}$$

The ozonides on treatment with water decompose with the rupture of the carbon chain at the original site of the double bond, during which an aldehyde group is formed at each carbon atom and hydrogen peroxide is liberated. This may be represented in either of two ways:

$$(1) \quad \begin{matrix} -CH\text{---}CH- \\ | \qquad | \\ O-O-O \end{matrix} + HOH \longrightarrow \begin{matrix} -CH \\ || \\ O \end{matrix} + \begin{matrix} -CH \\ || \\ O \end{matrix} + HOOH \qquad \text{or}$$

$$(2) \quad \begin{matrix} -CH-CH- \\ | \qquad | \\ O-O=O \end{matrix} \longrightarrow \begin{matrix} \quad\diagup O \diagdown \\ -CH \quad CH- \\ | \qquad | \\ O\text{----}O \end{matrix} +H_2O \xrightarrow{\qquad} 2 -CHO + H_2O_2.$$

Since the aldehyde thus formed is susceptible to oxidation it is attacked by the hydrogen peroxide to form carboxyl groups; hence it is usual to find a considerable portion of the aldehydes converted to acids during the hydrolysis of ozonides.

$$-CHO + HOOH \longrightarrow -COOH + HOH$$
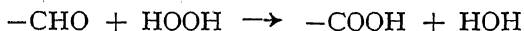
Continued action of ozone may cause oxidation along the fatty-acid chain with the formation of shorter chain fragments. This is particularly true if, during the hydrolysis of the ozonide, a stream of ozonized air is passed through the hydrolysis mixture, when it is found that an increasing amount of acid is formed even after hydrolysis of the ozonide is complete.

Air is probably the most common industrial reagent for oxidizing oils, owing to the ease of operation. If air is drawn or blown through oil at room temperature, oxidation proceeds slowly, destroying the colouring matter first; but finally the oil thickens and a gel is formed with the product remaining relatively light in colour. As the temperature is increased, the rate of reaction also increases until (for example, when pilchard oil is blown at 250°C.) rather abrupt changes occur in various properties. It is quite probable that the reactions which occur in the low and the high temperature blowing of oils are not the same, as the effect of higher temperatures on the peroxides first formed may cause their decomposition with liberation of oxygen. This oxygen will then attack other centres of unsaturation.

Blowing at high temperatures causes the apparent iodine value to decrease rapidly, dropping in the case of pilchard oil from 188 to 133 in six hours (Brocklesby and Denstedt 1934). The iodo-chlorides, indicating the presence of highly unsaturated acids, disappeared completely at the end of four hours' blowing.

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)xy-fatty acids showed little increase until after the fourth hour when the increase became more rapid and linear for the duration of the twenty-two hour reaction. The molecular weight increased steadily as also did the refractive index. These results are shown in figure 11.
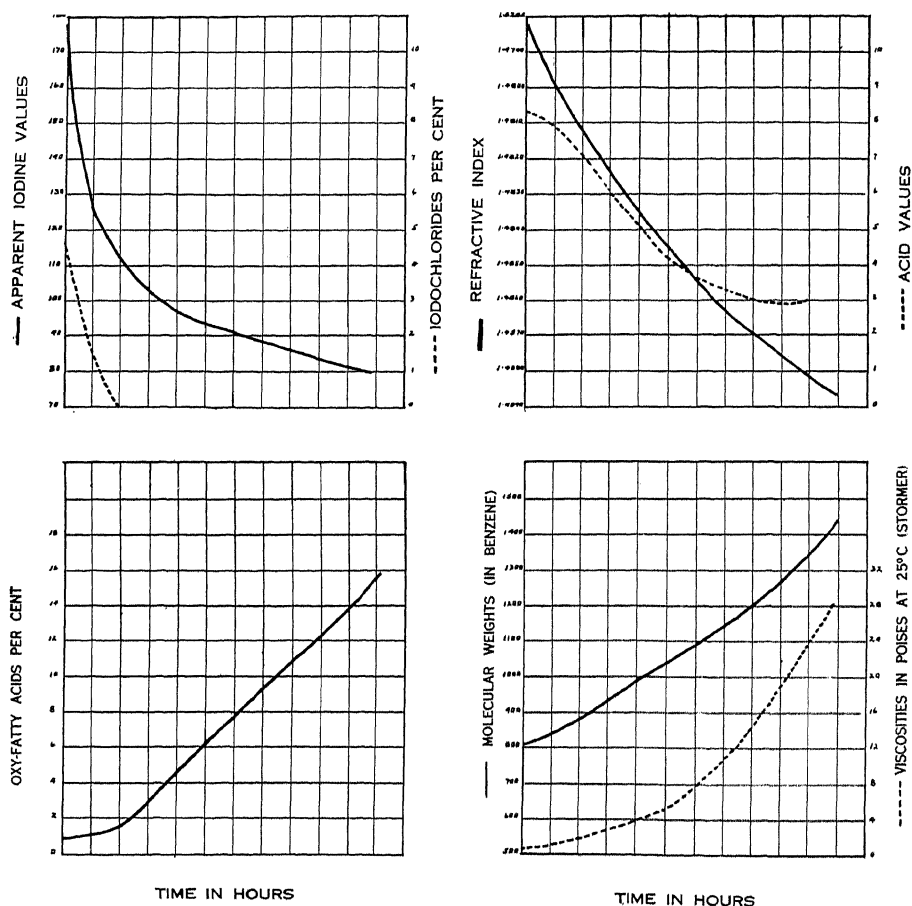

FIGURE 11. Changes in pilchard oil during blowing at 250°C.

In the drying of oil films oxidation plays a very important part. There is a preliminary induction period during which little oxygen is absorbed by the oil, but by the addition of catalysts or "driers" as they are called, or by certain refining processes, this period may be reduced or eliminated entirely.

The graph for the oxygen uptake of an oil (figure 12, A) is a characteristic S-shaped curve which is typical of autocatalytic reactions, that is, reactions in which the products catalyze the original reaction. Comparison of this curve

with curve B, which is the graph for the oxygen uptake of an oil to which a drier has been added, shows the elimination of the induction period.

It is generally accepted that the first step in the chain of oxidation reactions is the solution of oxygen in the oil followed by the formation of a loose compound (moloxide) with the dissolved oxygen, which can be removed at this stage under vacuum and elevated temperatures. This loose compound becomes a true peroxide and it is now generally agreed that two atoms of oxygen are absorbed for each double bond lost.

$$-CH=CH- \ + \ O_2 \qquad \begin{array}{c} -CH-CH- \\ \diagdown \diagup \\ O=O \end{array} \longrightarrow \begin{array}{c} -CH-CH- \\ | \quad | \\ O-O \end{array}$$
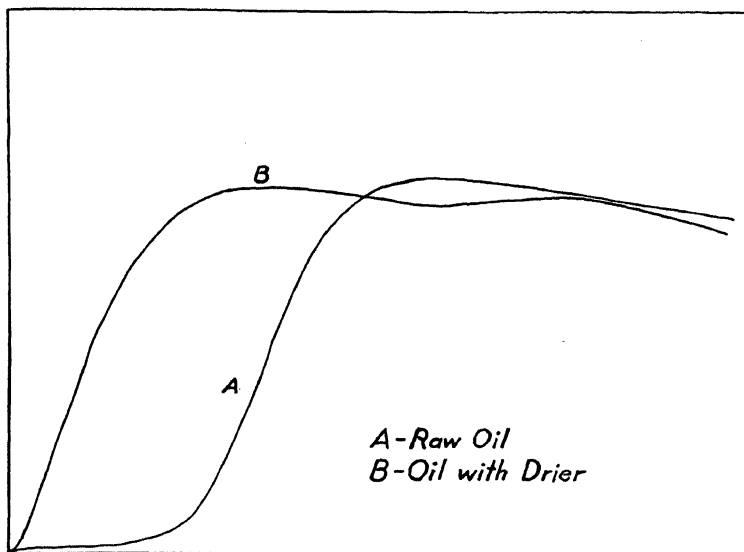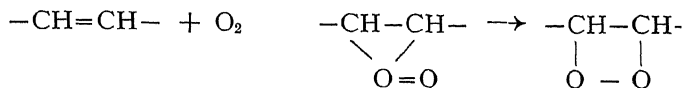
FIGURE 12.   Oxygen absorption.

The induction period was originally explained as being the time required for the formation of the peroxides, but, as a result of the work of Moureu and Dufraisse (1926), Holm, Greenbank and Deysher (1927), Hilditch (1930), and many others, it has been conclusively shown that naturally-occurring oils contain certain substances which inhibit the reaction of oxygen with the oil. These antioxidants, as they are called, have a greater affinity for oxygen than the oils have, consequently the oil is not attacked until the antioxidants have been oxidized. When the fatty acids of natural oils are converted into methyl esters and distilled, the antioxidants are removed and there is no induction period in the oxidation of the esters; certain refining processes also remove the antioxidants from oils (Denstedt and Brocklesby 1936).

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The many hydroxy, aldehydic, ketonic and acidic compounds isolated from oxidized oils indicate that the rearrangements and reactions that take place after the formation of the peroxides are very complex. The work of Ellis (1930) suggested, and the researches of Morrell and Phillips (1938) lend support to, the conception that ketohydroxy compounds are formed during the rearrangement of the peroxides. This takes place through a dihydroxy compound:

$$
\begin{array}{ccc}
\begin{array}{c} -CH-CH- \\ | \quad\; | \\ O\; - \;O \end{array}
&\longrightarrow&
\begin{array}{c} -C=C- \\ | \quad | \\ O \quad O \\ | \quad\; | \\ H \quad H \end{array}
&\longrightarrow&
\begin{array}{c} -CH-C- \\ | \quad\;\; || \\ O \quad O \\ | \\ H \end{array}
\end{array}
$$
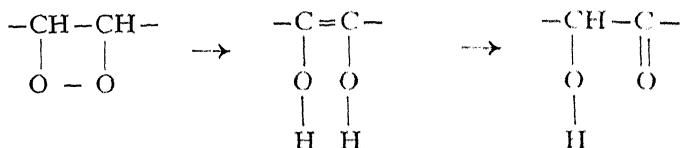
It is also apparent that different reactions occur, depending upon whether the oxidation takes place in the light or in the dark, where yellowing of the film appears. Since diketo stearic acid is yellow it is possible that the yellowing of oils containing linolenic acid is due to the formation of polyketo compounds or groupings, which are bleached again on exposure to light with the formation of polyhydroxy or ketohydroxy compounds (Elm 1932; Scheiber 1931; Eibner 1936).

When the reactions proceed farther than these stages, there is a rupture of the carbon chain with the production of various shorter chain compounds of aldehydic or acidic character such as nonylic and heptylic aldehydes [$CH_3(CH_2)_7$-CHO and $CH_3(CH_2)_5$CHO] and various lower fatty acids which cause the characteristic odours and flavours of rancid oil.

As previously mentioned, the introduction of driers brings about the direct addition of oxygen to the oils without the usual induction period. These driers are usually soluble salts or soaps, or oxides of metals such as cobalt, manganese, lead, etc., which can exist in more than one stage of oxidation, the lower stage being the more stable. These are incorporated into the oils using heat. Their value lies in bringing about the drying of paints more rapidly than would occur with the oil alone. While their action is not thoroughly understood at present, it appears that in addition to eliminating the induction period, they cause oxidation of the oils to take a somewhat different course as no peroxides are detected when driers are present. Apparently the oxidation proceeds directly to the stage beyond that of peroxide formation, and indeed may be of an entirely different character than when no catalyst is present. There is also continued oxidation even after the film has "dried" in the ordinary sense, that eventually causes failure of the film.

(d) POLYMERIZATION.

When unsaturated oils such as linseed, tung, pilchard and the like are heated to a suitable temperature in the absence of air or oxygen, they undergo several profound changes, the most characteristic of which is an increase in viscosity. The oil is said to have undergone "polymerization" and the chemical reactions

taking place are of importance, not only in the manufacture of heat-bodied oils for varnishes but also in the drying of oils to form solid films. The term "polymerization" in its widest and most modern sense means self-combination of similar molecules that are capable of reacting with each other to an almost indefinite extent (Carothers 1936). This definition does not entirely apply to the polymerization process taking place during the thickening of unsaturated oils because, as we shall see later, there appears to be a definite limit to the size of the polymerized molecules.

(i) HEAT POLYMERIZATION IN GENERAL

The heat treatment of drying oils is employed to produce a variety of products of use in the protective coating industries. In the manufacture of boiled oils, the oils are heated to about 220°C. (428°F.), solid driers added, and the heating continued until the driers have gone into solution. The use of liquid soluble driers permits lower temperatures to be employed, i.e. rarely in excess of 150°C. (302°F.), and the oils are usually given a mild blowing treatment with air. Semi-drying oils, such as soya bean, sunflower, etc., are given a more vigorous blowing with air during incorporation of the driers. The degree of polymerization resulting from the above processes is usually not as great as that obtained during the manufacture of stand oils. For the latter products, the oil may be heated in a direct-fired open kettle or in a more modern closed aluminium kettle heated by the cirulation of hot mineral oil or by electric coils. The oils are usually heated at 260° to 320°C. (500°-508°F.) until the desired "body" or increase in viscosity has been obtained, a process that may take several hours.

During the polymerization of drying oils, the hexabromide (or iodo-chloride) value falls rapidly and the iodine value less rapidly. The refractive index increases at approximately the same rate as the fall in iodine value, but in some cases may rise to a very high value during extensive treatment at high temperatures. Viscosity usually rises slowly during the period of rapid fall in iodine values, but subsequent to that period rises rapidly. With increase in viscosity there is usually an increase in molecular weight and in the amount of acetone-insoluble material. Polymerization of linseed oil takes place only at temperatures in excess of 240°C. (464°F.), but, as will be seen below, pilchard oil begins to polymerize at lower temperatures.

(ii) HEAT POLYMERIZATION OF FISH OILS

The changes taking place in a fish oil during heat treatment are shown in figure 13 taken from a paper by Brocklesby and Denstedt (1934) on the bodying of pilchard oil. The oil was a commercial sample that had been wintered at 6°C. (42.8°F.) and was polymerized in an electrically heated furnace in an inert atmosphere at the various temperatures indicated in the figure. Below 175°C. (340°F.) no detectable changes took place in the heated oil. From 175° to 200°C.(392°F.) there was a slow but uniform decrease in unsaturation. The apparent iodine values decreased very rapidly during the first 6 hours of heating at 250°C. (482°F.) after which the rate of decrease diminished greatly. As indicated by the iodo-chlorides, the rapid decrease in unsaturation was due to the elimination of some of the double bonds in the tetra- and penta-ethylenic fatty acids. The saturation of these acids to the tri- or di-ethylenic stage was complete at the end of the 8th hour at 250°C. and at the end of the 2nd hour at 300°C. (572°F.). Except for those of the 300°C.
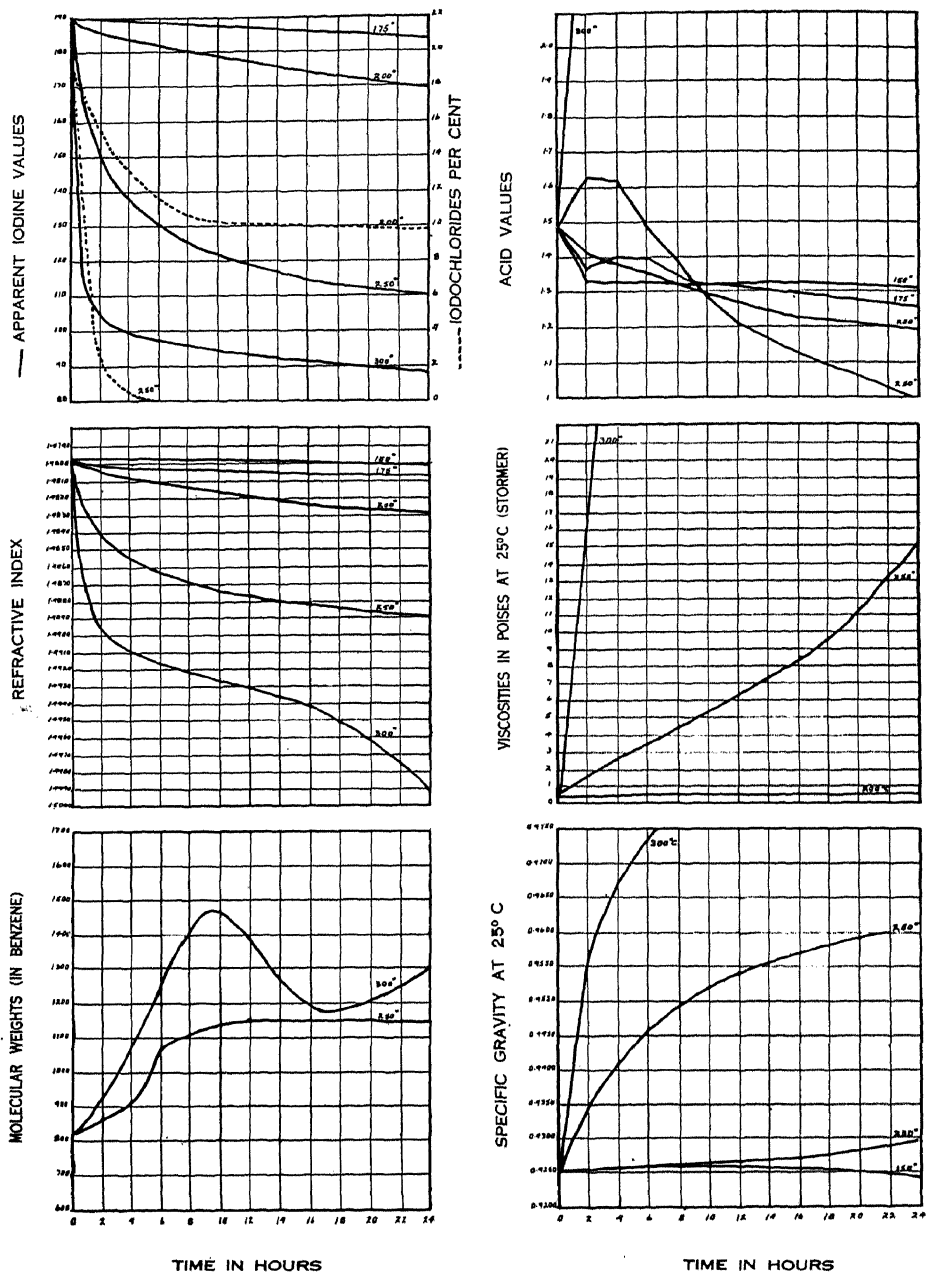
125

FIGURE 13. Heat polymerization of pilchard oil.

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run, the refractive indices showed similar changes to those of the apparent iodine values. At the higher temperature there was a rapid increase in these values after the 16th hour of polymerization. On reaching this point the oil gelled when cooled to 25°C. (77°F.).

The acid value of the oil decreased in runs up to 200°C., probably due to the volatilization of the small amounts of free fatty acids originally present in the oil. In the 250°C. run the acid value increased up to the 4th hour and then dropped rapidly. It would appear either that the fatty acids are recombined after a certain stage in the heating, or that after the initial period of acid formation the rate decreases and those that are formed are distilled off. No large increases in the amount of volatilized acidic by-products were noted, however. Decomposition at 300°C. was very extensive; the acid value rose rapidly and at the 16th hour reached a value of 18.

All samples from the 300°C. run and the last one of the 250°C. run deposited a white flocculent precipitate on standing for some time at room temperature. The amount of this deposit was not proportional to the acid value of the samples and proved, on analysis, to be neutral solid glycerides that had crystallized out in increasing amounts as bodying proceeded.

Decomposition of the oil was relatively slight below 200°C., and the volatile products consisted chiefly of acidic, aldehydic and ketonic substances with traces of hydrocarbons. At higher temperatures, the decomposition was relatively greater and the products gradually became more acidic in nature. The condensed distillate from the runs at 250° and 300°C. consisted chiefly of free fatty acids with a neutralization value of about 270 and an iodine value of 90. The substance melted at 18°C. (64.4°F.) and appeared to be a mixture of iso-acids of the C_{16} and C_{18} series.

As with the other analytical data, there was no significant change in viscosity until the 250°C. run, when it increased linearly until the 16th hour, reaching a value of 8 poises. Thereafter, increase in viscosity was more rapid, reaching 15 poises at the 24th hour. At 300°C. increase in viscosity was very rapid, the 6th hour sample gelling quickly at 25°C.

From these data it can be concluded that the critical temperature for the heat-polymerization of pilchard oil lies between 250° and 275°C. (482°and 527°F.). Above the latter temperature considerable decomposition takes place, and an examination of the fatty acids from the 300°C. (572°F.) run indicates that in addition to polymerization a certain amount of condensation also contributes to the general reaction.

The Los Angeles Paint and Varnish Club (Behr, Sliger, McLean and Smith 1937) have reported an interesting study of the heat-bodying of sardine oil. The sample used in the investigation was an alkali-refined, bleached and wintered California sardine oil with an iodine value of 200 and a chill test of 8 hours at 0°C. (32°F.). As a result of the work on this oil, these investigators recommend that such highly refined sardine oils should be bodied at a maximum temperature of 280°C. (535°F.), three hours being allowed to reach a temperature of 249°C. (480°F.) and an additional two hours to reach 280°C. They further recommend that a maximum viscosity of 9 poises should be specified for these oils. Under these conditions they claim that "the polymerization of the unsaturated glycerides is carried to a reasonable degree of completeness with a minimum gel structure and without the development of polymer cloud". According to these authors the formation of a cloudy haze or actual precipitate in bodied fish oils is not due to saturated glycerides but to coagulated gel particles that are insoluble at room temperature in the kettled oil. This explanation of the polymer cloud does not entirely coincide with the present writer's experience. The fact is, as admitted by the above authors, the rate of formation and amount of this polymer cloud is proportional to the amount of stearine in the oil and also to

the amount of polymerization. The lower the cloud point of the wintered oil, the more polymerization it will stand before this cloudy appearance is noticed. The fact that the most highly wintered oils still show this cloudiness is no proof that it is not stearine because the most efficient wintering methods cannot remove all the stearine from a fish oil. Furthermore, if a polymerized oil is given a high-temperature steam distillation treatment that removes the greater part of the saturated fatty acids the resulting polymer does not show this cloudiness to the same extent. Final proof lies in the actual examination of the precipitated material which in the writer's case proved to be largely saturated glycerides. Although the formation of insoluble gel particles may in part be the cause of the polymer cloud, the writer is of the opinion that it is largely due to precipitated stearine which progressively becomes more and more insoluble in the polymerized oil. There is also some evidence, admittedly meagre, to show that during the heat treatment of fish oils there is a rearrangement of the fatty acids to form a larger proportion of completely saturated glycerides, a circumstance that would, of course, enhance the rate of formation of the polymer cloud.

Another matter of interest in regard to the heat-polymerization of fish oils is the effect of stearine on the rate and extent of polymerization. Behr (1936) has given some interesting data along these lines. In the first place he finds that a crude sardine oil contained 22 per cent saturated fatty acids and the same oil, after being wintered to stand a cloud test of 20 hours at 0° C. (32° F.), still contained 17 per cent saturated acids. Further cold clearing so that the oil would stand 100 hours at 0° C. only reduced the saturated fatty acid content to about 16.75 per cent, but the loss through the removal of stearine was very high (Section 8 I (b), cold clearing). A sample of crude sardine oil was lightly winterized so that it would stand a chill test of 0.5 hours at 0° C.; a sample of the same oil was further winterized to stand a chill test of 20 hours and a third sample of the crude oil had added to it some of the stearine removed from the first two samples. The three lots were then polymerized under identical conditions. Measurements of the viscosities and acetone-insoluble contents of the three samples showed that the degree of polymerization was very much greater in the case of the 20-hour chill-test oil than in the 0.5-hour chill-test oil, which in turn was greater than that of the oil which had had stearine added to it. These results are in harmony with those of the writer, in which a sample of Canadian pilchard oil was cold-cleared to various degrees and the various samples simultaneously polymerized in an inert atmosphere. The data are as given in table XIX. The retarding effect of stearine on the heat-polymerization of the oil is very marked and indicates the necessity for the cold clearing of fish oils that are to be used in the manufacture of bodied oils.

Work, Swan, Wasmuth and Mattiello (1936) reported the changes in physical and chemical properties of menhaden oil during heat-bodying. The results were much the same as those found by Brocklesby and Denstedt (1934) for pilchard oil, the greater rate of decrease of hexabromide values as compared with that of iodine values again being emphasized.

TABLE XIX. Effect of stearine on polymerization of pilchard oil

Sample	Stearine removed (%)	Cloud-test clear oil, A.C.S. method (°C.)	Molecular weight, polymerized oil, Rast's method
B	7.0	0.9	867
D	11.2	−1.0	1256
E	15.0	−2.3	1470
I	27.8	−5.0	1790

(iii) POLYMERIZATION BY OTHER AGENCIES

Polymerization of drying oils can be brought about by agencies other than heat. Stannic chloride at low temperatures causes such oils to thicken considerably, the amount of thickening depending upon the quantity of stannic chloride used. Aluminium and antimony trichlorides act in the same way, forming thick dark products. The action of these three agents is not only to promote polymerization but also condensation, the carboxyl group of the fatty acids being involved in the reaction. Other reagents have been used that have a catalytic effect on the actual polymerization process. Sulphur dioxide gas has an accelerating effect on the heat-polymerization of oils (Waterman and van Vlodrop 1936) and also on the nature of the solid dried films (Brocklesby and Denstedt 1933). The catalytic action of sulphur and selenium on the heat-polymerization of drying oils was shown by Waterman, van Vlodrop and Althusius (1938), who heat-treated linseed oil in the presence and absence of small amounts of these elements. It was shown that 0.3 per cent was sufficient to have an appreciable effect on the molecular weight of the polymerized oils, and that oils polymerized in the presence of sulphur and selenium remained completely clear at room temperature, a behaviour in contrast to that of the polymerized oil prepared under the same conditions without these elements. Sulphur chloride (S_2Cl_2) also acts as a polymerizing reagent, but in this case the sulphur actually acts as a link between the polymerized fatty acids. This reaction is discussed more fully under the section dealing with the addition of sulphur to drying oils. Of the remaining metals or metallic oxides that have an effect on the polymerization of oils (other than the oxidizing catalysts, i.e. driers) mention should be made of the action of nickel and platinum, which at 200° C. (392° F.) bring about a rearrangement of the double bonds in unsaturated fatty acids to the conjugated position (Waterman and van Vlodrop 1936), after which polymerization takes place.
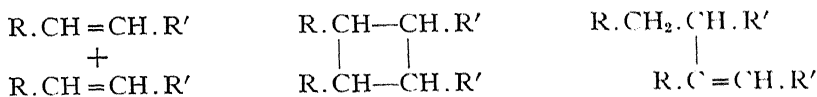
(iv) THEORIES OF POLYMERIZATION

Although our knowledge of the mechanism of the polymerization of unsaturated oils and that of film formation is still far from complete, certain concepts have been developed during the past few years that have helped to clarify the situation. It has been stressed that polymerizations are but "the ordinary reactions of organic chemistry which are proceeding in multiple fashion

because of the multiplicity of reactive or functional groups present in the structure of the polymerizing substance" (Bradley 1937). As far as fish oils are concerned the reactive groups are the unsaturated bonds of the fatty acids, although it must be kept in mind that during heat treatment or air-drying of films some hydrolysis may occur, in which case the carboxyl group of the fatty acid may also become a reactive group. All double bonds may not be of equal reactivity, since it is known that in poly-unsaturated fatty acids the apparent reactivity of the double bonds increases with the distance away from the acid or carboxyl group.

The great reactivity of conjugated double bonds is exemplified by the ease of polymerization of tung oil, the chief characteristic component of which is elaeostearic acid containing three double bonds in a conjugated system. It has recently been postulated that other unsaturated oils, originally not containing conjugated double bonds, undergo isomerization during heat treatment in which conjugated bonds are produced; these then undergo polymerization. It must be admitted, however, that absolute proof is yet to be obtained, but the advent of better methods for the determination of conjugated systems and the application of these methods to polymerized oils seem to indicate that such conjugation does precede actual polymerization.

The actual structure of the polymers also has yet to be determined, but the most likely course of the reaction is for two double bonds to react to form an unstable four-carbon atom ring, which breaks open and rearranges to give a chain compound with one double bond still intact. This scheme is shown as follows:

$$R.CH=CH.R' \qquad R.CH\!-\!CH.R' \qquad R.CH_2.CH.R'$$
$$+ \qquad\qquad |\quad\ | \qquad\qquad\qquad |$$
$$R.CH=CH.R' \qquad R.CH\!-\!CH.R' \qquad R.C=CH.R'$$

This type of reaction may take place between two unsaturated fatty acids both attached to the same glyceride molecule (intra-molecular) or between fatty acids of different glyceride molecules (inter-molecular). In the second case, of course, an increase in molecular weight takes place.

Difference in structure between a soluble and/or fusible polymer, such as those present in a bodied oil, and a solid, insoluble and/or infusible gel is now thought to lie in the actual space structure. The former type is held to be linear or two-dimensional and the latter a cross-linked or three-dimensional form. Neither the free fatty acids of drying oils nor their ethyl or glycol esters are air-drying or convertible by heat into solid polymers unless condensation reactions take place, whilst the glycerides are both air-drying and heat-convertible by reason of the ease with which cross-linking can take place. The heat-polymerization of an unsaturated oil therefore involves the formation of linear polymers in which the molecules are held together either by a ring structure or by a single bond. Usually the polymerization does not extend beyond the dimeric stage, in which two glyceride molecules are held together by the inter-

molecular reaction between an unsaturated bond in each glyceride molecule. Intra-molecular reactions may take place simultaneously.

In the air-drying of films the formation of peroxides occurs as the first step. The amount of oxygen absorbed before actual gel formation takes place depends upon the structure of the oil and the amount of heat-polymerization it has previously undergone. Just how the peroxides decompose and bring about polymerization or condensation is not definitely known, but it is realized that the drying process becomes "only a mechanism in which an essentially linear and usually liquid polymer is converted into a cross-linked or three-dimensional polymer" (Bradley 1937). The agent necessary to bring about this conversion may be considered as "the converting agent or as the converting promoter."

Polymerized oils, both liquid and solid, exhibit certain chemical properties that differentiate them sharply from non-polymerized oils. The behaviour towards the hydrogenation process and halogenating reagents might be briefly mentioned here. It has been shown that the intra-molecular polymerization products can be hydrogenated; presumably their ring structure is not stable. The inter-polymerized material resists hydrogenation; repeated attempts in these laboratories to reduce the molecular weight of polymerized methyl, ethyl and glycerol esters of unsaturated fatty acids by means of hydrogenation in the presence of nickel, platinum and palladium have failed. Thus when a heat polymerized oil is hydrogenated, hydrogen is absorbed by the free unsaturated bonds and by those produced by the rupture of the intra-polymerized group; the proportion of saturated fatty acids increases, but the molecular weight remains approximately unchanged.

The behaviour of polymerized oils towards halogenating reagents is totally dissimilar to that of unpolymerized oils; the absorption is relatively slow and the reaction never appears to reach equilibrium. The slow rate of absorption is not dependent on the presence of a three-dimensional polymer, for the polymerized acids (linear polymers) isolated from a polymerized oil still exhibit the slow absorption. It has been proven in these laboratories that considerable substitution takes place when iodine mono-chloride or other analytical halogenating reagents are allowed to react with polymerized oils; consequently, iodine values have but little meaning as a measure of unsaturation when applied to these materials. Finally, it is of interest to note that brominating reagents always give higher absorption values than do mixed halogenating reagents such as iodine monochloride. Thus, pyridine sulphate dibromide, which usually gives lower absorptions than iodine monochloride with unpolymerized oils, always gives absorptions from 10 to 20 per cent higher when applied to the polymerized products. So far these peculiar effects of halogenating reagents have not been satisfactorily explained, but it can readily be seen that the so-called "iodine values" of polymerized oils or esters of unsaturated fatty acids cannot be relied upon to the same extent as those of the non-polymerized substances.

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(e) CONDENSATIONS.

This discussion of condensations involving fatty acids or their esters is restricted to those reactions in which a non-fatty material is one of the reactants; condensations taking place when oils are heat-treated or oxidized are not included.

By the use of the proper condensing agents it is possible to introduce phenols at the double bond of unsaturated fatty acids or their esters. The reaction proceeds in two steps, the intermediate compound formed being an aromatic ether which then rearranges to form a substituted phenol as follows:

$$CH_3.(CH_2)_7.CH:CH.(CH_2)_7.COOH + C_6H_5OH \rightarrow CH_3.(CH_2)_7.CH.CH_2.(CH_2)_7.COOH$$

$$\underset{\text{Oleic acid}}{} \qquad \underset{\text{Phenol}}{} \qquad \underset{\text{Ether, or intermediate compound}}{O.C_6H_5}$$

$$CH_3.(CH_2)_7.CH.CH_2.(CH_2)_7.COOH$$
$$|$$
$$C_6H_4.OH$$

10-hydroxy phenyl stearic acid
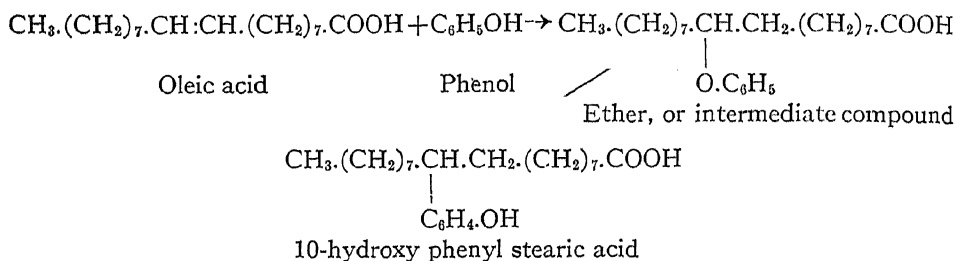
This reaction may be carried out with a variety of phenols and different fatty acids of varying iodine value (Niederl and Liotta 1933).

Using pilchard oil (iodine value 164) and phenol with dry hydrogen chloride as condensing agent, the writer obtained a product of iodine value 11 in which 93 per cent of the double bonds were saturated with phenol. Fifty per cent of the phenyl ethers were rearranged to the hydroxy phenyl stearic acid, the remainder being unchanged. Similar results were obtained using cresol and ·pilchard oil.

By suitable control of the reaction, there may be obtained from pilchard oil a product which contains phenol groups but retains sufficient unsaturation to dry to a film when dissolved in a thinner, mixed with a cobalt drier and exposed to the air. While this product is not resistant to water it might have a use as a bactericidal protective coating under less drastic conditions.

In the glyptal type of resin, which is prepared by the condensation of phthalic anhydride with glycerol, the resin may be modified by the introduction of fatty acids to take the place of a part of the phthalic anhydride. This renders the resin more soluble in oils and also makes it more plastic. If fatty acids from drying oils are used, the resin will also possess some air-drying properties. The process is accomplished by heating a suitable mixture of glycerol (3 equivalents) with phthalic anhydride (2.5 equivalents) and fatty acids (0.5 equivalents) until the water formed by the reaction ceases to be liberated. Some results obtained in these laboratories with linseed and pilchard oil fatty acids are given in the section dealing with the utilization of fish oils in paints and varnishes.

The success of the new type of detergents, the sulphonated alcohols, and the difficulties in securing the alcohols have led to an artful method of obtaining

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a sulphonated product with much the same properties. The acid group of fatty acids is condensed with a nitrogenous compound such as ethanolamine to give a substituted amide with a free alcohol group which can then be sulphonated to give a suitable detergent or wetting agent. The general reaction is as follows:

$$CH_2.NH_2 + HOOC.(CH_2)_7.CH:CH.(CH_2)_7.CH_3 \rightarrow CH_2.NH.OC.(CH_2)_7.CH:-$$

$$| \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad | \qquad CH.(CH_2)_7.CH_3$$

$$CH_2.OH \qquad\qquad\qquad\qquad\qquad\qquad \overset{H_2SO_4}{\diagup} \; CH_2.OH$$

Ethanolamine   Oleic acid   ↙   Substituted amido-ethanol

$$CH_2.NH.OC.(CH_2)_7.CH:CH.(CH_2)_7.CH_3$$

$$|$$

$$CH_2.O.SO_3H$$

Substituted amido-ethanol sulphate
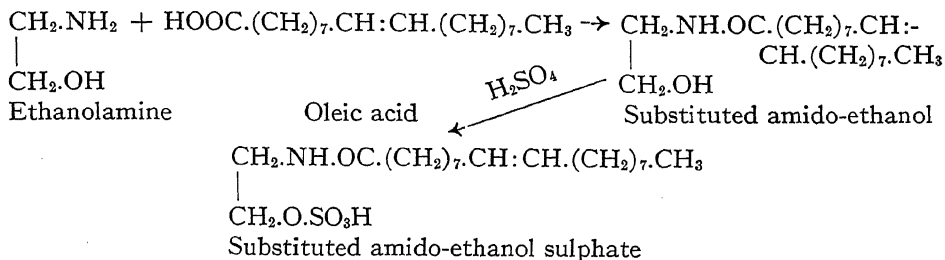
Many variations of this type of reaction have been patented in which the carboxyl group of the fatty acid is condensed with a substance having one or more alcohol groups, the latter then being sulphonated and the sulphonated product neutralized with an alkali to form the alkali salt. The use of poly-ethylenic fatty acids from fish oils opens up many possibilities along these lines for, in addition to sulphonation of the alcohol group, the unsaturated bonds also are sulphonated as described under sulphonation.

It is possible to bring about a "Friedel-Crafts" reaction between aromatic substances such as benzene, phenol, etc., and unsaturated acids by using aluminium chloride as the condensing agent. Although these compounds have not been investigated to any great extent, preliminary experiments indicate that some interesting products can be made from highly unsaturated fatty acids by this reaction.

The condensation of fatty acids with abietic acid resins has been utilized to give oil gels that may be used in the preparation of floor tiles and roofing compounds. This provides a material that permits the use of lighter colours than is possible with fatty acid pitches.

(*f*) SULPHATION AND SULPHONATION.

Sulphation and sulphonation are processes employed to make fatty oils, fatty acids and fatty alcohols compatible with water, thus widening the application of these fatty materials in industrial arts. Such processes were applied to olive oil as early as 1834, and achieved industrial significance with their application to castor oil in 1875 to form the "Turkey red oil" used for applying alizarin dye to cotton.

Fatty oils and alcohols having more than six carbon atoms in the hydrocarbon portion of the molecule are practically insoluble in water and in cold, dilute, aqueous solutions of alkalies or inorganic acids; fatty acids of similar constitution are likewise practically insoluble in water and acids, but react with alkaline solutions to give colloidal solutions of soaps. Sulphation or sulphonation renders all of these three types of fatty substances capable of forming colloidal solutions with water and thus makes their valuable inherent properties available in neutral or

acid aqueous media. In alkaline media, soap-like compounds are formed which have valuable properties not possessed by ordinary soaps; such compounds are referred to by the general term "detergents" rather than by the term "soaps", which indicates a special class of detergents. The particularly interesting detergent properties of sulphated or sulphonated fatty alcohol derivatives have, during the past ten years, greatly stimulated industrial interest in the fatty alcohols obtainable directly from marine mammalian waxes (e.g. spermaceti) and indirectly through the hydrogenation of fatty acids obtainable from all marine animal oils.

The distinction between sulphation and sulphonation is set forth below, followed by an enumeration of the reactions involved, the general properties of the resulting types of products and examples of their technical applications. The application of the processes to marine oils is given in Section 8 II (e), and further reference to their utilization will be found under several headings in Section 9.

When a fat, fatty oil, unsaturated fatty acid or a fatty alcohol is treated with strong sulphuric acid, the ensuing process of *sulphation* yields, among other products, *sulphated* fatty compounds, chemically termed fatty half-*esters* of sulphuric acid, in which the sulphur atom is linked through an oxygen atom to a carbon atom of the fatty constituent: $-HC-O-SO_2OH$.

When, however, sulphur trioxide, oleum, pyrosulphuric acid, or certain sulphuric acid derivatives such as chlorosulphonic acid are used in treating fatty substances, a process of *sulphonation* takes place resulting in *sulphonated* fatty compounds, in which the sulphur atom is linked directly to a carbon atom of the fatty constituent: $-HC-SO_2OH$.

Unfortunately the processes of *sulphation* and *sulphonation*, and the respective sulphated and sulphonated products (*sulphates* and *sulphonates*) are frequently confused in commercial practice (Hecking 1938). The term "sulphonation" is generally applied, even when sulphated products are known to result. In this Bulletin the distinction will be maintained wherever the nature of the product is reasonably certain.
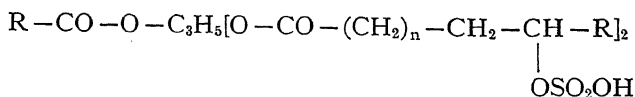
(i) SULPHATION OF FATS

The sulphation of fats (which include the fatty oils) leads to a series of complex reactions. The primary action of sulphuric acid on unsaturated fats is that of sulphation of one or more of the double bonds:

$$-HC=CH- \qquad \text{Double bond} \qquad -CH_2-CH-$$
$$+ \qquad\qquad + \qquad \longrightarrow$$
$$H-O-SO_2OH \quad \text{Sulphuric acid} \qquad\qquad O-SO_2OH$$
$$\text{(H}_2\text{SO}_4) \qquad \text{Sulphated product}$$
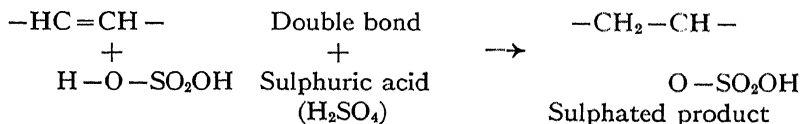
the extent of the sulphation being governed by the number and nature of the unsaturated fatty acid components of the glyceride.
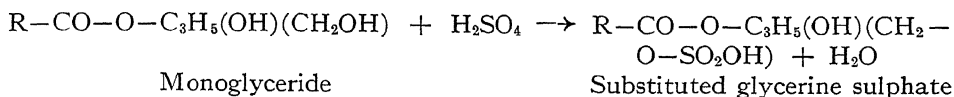
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$$R-CO-O-C_3H_5[O-CO-(CH_2)_n-CH=CH-R]_2 \quad + \quad 2\,H_2SO_4 \quad \longrightarrow$$
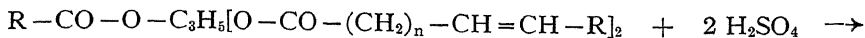
A fat glyceride containing at least
two unsaturated constituents

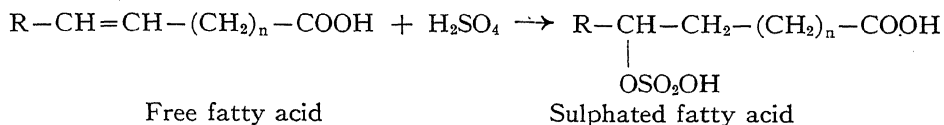$$R-CO-O-C_3H_5[O-CO-(CH_2)_n-CH_2-CH-R]_2$$
$$|$$
$$OSO_2OH$$

A di-sulphated glyceride.

Depending on the sulphating conditions, which are discussed more fully under Section 8 II (*e*), the reaction usually proceeds further (Hart 1937).
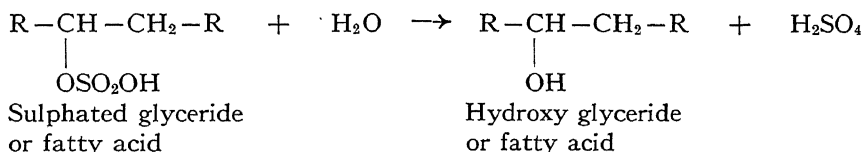
A portion of the fat may become partially or completely hydrolyzed to glycerine, mono- or di-glycerides and free fatty acids. The alcoholic groups of the glycerine, mono- or di-glycerides may become sulphated:

$$R-CO-O-C_3H_5(OH)(CH_2OH) + H_2SO_4 \longrightarrow R-CO-O-C_3H_5(OH)(CH_2-$$
$$O-SO_2OH) + H_2O$$

Monoglyceride $\qquad\qquad$ Substituted glycerine sulphate

and at least some of the unsaturated fatty acids liberated by the hydrolysis are sulphated:

$$R-CH=CH-(CH_2)_n-COOH + H_2SO_4 \longrightarrow R-CH-CH_2-(CH_2)_n-COOH$$
$$|$$
$$OSO_2OH$$

$\qquad$ Free fatty acid $\qquad\qquad$ Sulphated fatty acid

The sulphated fat and fatty acids are not very stable in the presence of sulphuric acid and certain impurities bound to be present, and a second type of hydrolysis takes place at the position of sulphation:

$$R-CH-CH_2-R \quad + \quad H_2O \quad \longrightarrow \quad R-CH-CH_2-R \quad + \quad H_2SO_4$$
$$|\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$OSO_2OH \qquad\qquad\qquad\qquad\quad OH$$

Sulphated glyceride $\qquad\qquad$ Hydroxy glyceride
or fatty acid $\qquad\qquad\qquad\quad$ or fatty acid

The hydroxy glycerides may remain as such, or may undergo a very complicated condensation or polymerization. The hydroxy fatty acids, depending on the temperature of the sulphation process, may or may not undergo dehydration to *lactones:*

$$R-CH-(CH_2)_n-CO \qquad\qquad R-CH-(CH_2)_n-CO$$
$$|\qquad\qquad\qquad |\qquad \longrightarrow \quad |\qquad\qquad\qquad | \quad + \quad H_2O$$
$$OH\qquad\qquad HO \qquad\qquad\qquad\quad \underline{\qquad\qquad}O$$

$\quad$ Hydroxy fatty acid $\qquad\qquad\qquad$ Fatty acid lactone
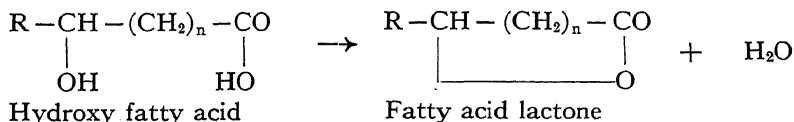
or condensation to *lactides:*

$$
\begin{array}{cc}
R-CH-(CH_2)_n-CO & R-CH-(CH_2)_n-CO \\
\quad| \qquad\qquad | & \quad| \qquad\qquad\qquad | \\
OH \qquad\quad HO & O \qquad\qquad\qquad O \quad + \quad 2H_2O \\
OH \qquad\quad HO & \quad| \qquad\qquad\qquad | \\
\quad| \qquad\qquad | & OC-(CH_2)_n-HC-R \\
OC-(CH_2)_n-HC-R & \\
\text{2 molecules of hydroxy} & \text{Fatty acid lactide} \\
\text{fatty acid} &
\end{array}
$$
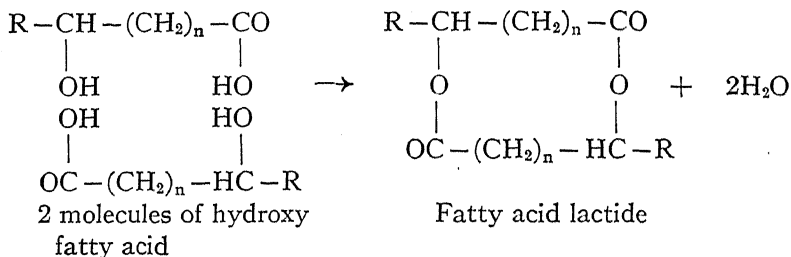
The sulphation of a commercial fat may therefore result in a mixture of most or all of the following substances:

Partially or completely sulphated triglycerides; partially hydrolyzed unsulphated glycerides; glycerine; free fatty acids; sulphated glycerine and its fatty acid esters; sulphated fatty acids; hydroxy acids; lactones; lactides; polymerized products.

The proportions of the above compounds vary with the nature of the fat and the sulphating process, and although a high yield of true sulphated fat is desirable, some of the by-products remaining in the finished oil confer upon it certain properties suitable for special applications.

(ii) SULPHATION OF FATTY ACIDS

The sulphating of fatty acids and the secondary reactions leading to the production of hydroxy fatty acids, fatty acid lactones and lactides have already been described under (i) above. It has recently been shown (Steger, van Loon, Vellenga and Pennekamp 1938) that, during sulphation of some double bonds, the $-O-SO_2OH$ group may attach itself to either carbon atom:

$$
\begin{array}{ccc}
R-CH_2-CH-(CH_2)_nCOOH & & R-CH-CH_2-(CH_2)_nCOOH \\
\qquad\quad | & \text{or} & \quad| \\
\qquad OSO_2OH & & OSO_2OH
\end{array}
$$
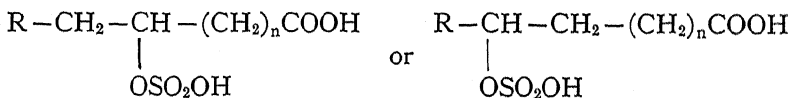
Experiments with various oils sulphated under conditions as nearly identical as possible have shown that these secondary reactions take place with some fatty acids more readily than others; sulphated oleic acid tends to form hydroxy oleic acid and some lactone, whereas the hydroxy acids formed from sulphated whale oil tend to pass completely into the lactone form (Sunderland 1935). In general, the hydrolysis of sulphated fatty acids to hydroxy acids is hindered by low sulphation temperatures (Riess 1931).

(iii) SULPHATION OF FATTY ALCOHOLS

The sulphation of a fatty alcohol takes place as follows:

$$
CH_3-(CH_2)_{16}-CH_2O-H + HO-SO_2OH \rightarrow CH_3-(CH_2)_{16}-CH_2O-SO_2OH + H_2O
$$
$$
\text{Stearyl alcohol} \qquad \text{Sulphuric acid} \qquad \text{Stearyl sulphate} \qquad \text{Water}
$$
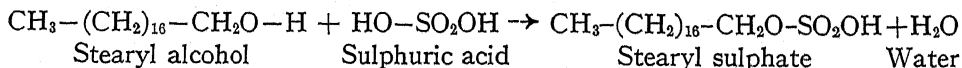
and is therefore an esterification (to a half-ester of sulphuric acid) instead of a straight addition reaction as in the case of sulphation of a double bond.

If the fatty alcohol is unsaturated, it has been shown (Riess 1931) that simultaneous sulphation of the double bond and alcohol group takes place:

$$CH_3-(CH_2)_7-CH=CH-(CH_2)_7-CH_2OH+2H_2SO_4 \longrightarrow$$

Oleyl alcohol

$$CH_3-(CH_2)_7-CH_2-CH-(CH_2)_7-CH_2O-SO_2OH$$

$$|$$
$$OSO_2OH$$

Sulphated oleyl sulphate
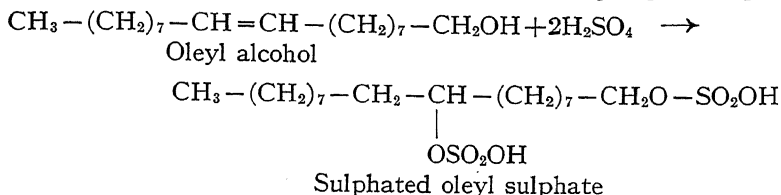
The sulphation of the double bond takes place more slowly than in the case of unsaturated fatty acids, and the central sulphate group does not hydrolyze to the corresponding hydroxy compound as readily as in the case of the sulphonated acid [see (i) above].

Several other reactions for producing these commercially important sulphated fatty alcohols are known, involving the use of sodium pyrosulphate (or sulphur trioxide) in the presence of pyridine.

(iv) SULPHONATION OF FATTY COMPOUNDS

Sulphonation may be achieved in many ways; the commonest sulphonating agents being sulphur trioxide (SO_3), oleum (concentrated sulphuric acid containing sulphur trioxide and approximating the composition of pyrosulphuric acid, $H_2S_2O_7$), and chlorosulphonic acid ($Cl-SO_3H$). These may be used alone, though usually in the presence of a diluting, inert organic solvent. The general reaction may be formulated as:

$$-CH=CH- \quad + \quad SO_3 \longrightarrow \quad -CH=C-$$

$$|$$
$$SO_3H$$
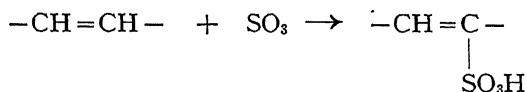
though the actual action of most sulphonating agents is more complex and leads to saturation of the double bond as well as sulphonation. Sulphuric acid in the presence of acetic anhydride is also employed, and some authorities state that sulphuric acid alone sulphonates unsaturated fatty compounds thus:

$$-CH=CH- \quad + \quad HO-SO_3H \longrightarrow \quad -CH-CH-$$

$$| \quad |$$
$$HO \quad SO_3H$$
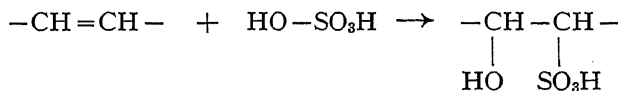
Saturated fats and fatty acids are sulphonated by chlorosulphonic acid as follows:

$$R-CH_2-R \quad + \quad Cl-SO_3H \longrightarrow \quad R-CH-R \quad + \quad HCl$$

$$|$$
$$SO_3H$$
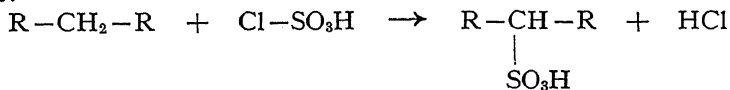
Some types of sulphurized fats page 142 [e.g. $R-CH(SH)-R$], may be oxidized to sulphonates [$R-CH(SO_3H)-R$] by direct addition of three atoms of oxygen between the sulphur and hydrogen.

Sulphonated fatty alcohols may be prepared by certain of the above reactions, as well as from the sodium salts of sulphated fatty alcohols:

$$R-OSO_2ONa \quad + \quad Na_2SO_3 \quad \rightarrow \quad R-SO_3Na \quad + \quad Na_2SO_4$$

| Sodium salt of sulphated fatty alcohol | Sodium sulphite | Sodium salt of fatty sulphonic acid | Sodium sulphate |
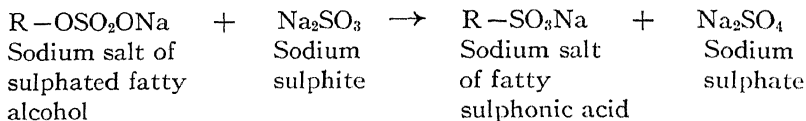
(v) SULPHATED AND SULPHONATED DERIVATIVES OF FATTY COMPOUNDS

A great many new detergents and textile finishers placed on the market during the past ten years have been developed by condensation of fatty acids or alcohols with other chemicals already sulphated or sulphonated:

$$C_{17}H_{33}CO-OH \; + \; HO-CH_2CH_2SO_3Na \; \rightarrow \; C_{17}H_{33}CO-O-CH_2CH_2SO_3Na$$

| Oleic acid | Sodium salt of isethionic acid | Sulphonated fatty acid ester ("Igepon A"). $+H_2O$ |

$$C_{17}H_{33}CO-Cl \; + \; H-NH-CH_2CH_2OSO_2OH \; \rightarrow \; C_{17}H_{33}CO-NH-CH_2CH_2O-SO_2OH+HCl$$

| Oleyl chloride | Sulphuric ester of amino ethyl alcohol | Sulphated substituted amide ("Igepon T") |

$$
\begin{array}{c}
C_8H_{17}OH \\
+ \\
C_8H_{17}OH
\end{array}
\quad
\begin{array}{c}
HOOC-CH_2 \\
| \\
HOOC-CH-SO_3Na
\end{array}
\quad \rightarrow \quad
\begin{array}{c}
C_8H_{17}O-CO-CH_2 \\
| \\
C_8H_{17}O-CO-CH-SO_3Na
\end{array}
\quad +2H_2O
$$

| 2 molecules of octyl alcohol | Sodium sulpho-succinate | Sulphonated di-ester of fatty alcohol ("Aerosol OT Dry") |

A great number of other such commercial products is listed by van Antwerpen (1939).

(vi) PROPERTIES OF SULPHATED AND SULPHONATED FATTY COMPOUNDS

Sulphation and sulphonation of unsaturated fatty compounds evidently cause certain unsaturation characteristics, such as iodine value, drying properties, tendency toward rancidity, ability to be hydrogenated, etc., to diminish in proportion to the original number of double bonds saturated with the sulphuric acid or similar reagent. These changes in properties are, however, secondary to other important changes in properties resulting from the introduction of the $-O-SO_2OH$ or $-SO_3H$ groups.

These groups in a fatty molecule allow the molecule to be attracted by water at their point of introduction, while the remainder of the molecule retains its property of miscibility with oils. Consequently, sulphated and sulphonated fatty materials act as intermediaries or emulsifying agents for the production of emulsions or creams from water and water-insoluble oils and greases, thus permitting

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industrial applications of mineral oils where the use of such oils alone would be impracticable. This "wetting" property also allows the penetration of fatty materials into moist substances, and causes sulphated and sulphonated oils to be valuable carriers of water-soluble dyes to materials not readily wet by water (see Section 9).

The development of sulphated and sulphonated fatty compounds can also be traced largely to industrial dissatisfaction with soaps as used for various purposes. Ordinary soaps, being salts of weak (fatty) acids and strong bases (sodium or potassium alkalies), hydrolyze in water and show an alkaline reaction which is undesirable for many purposes. If an attempt is made to overcome the alkaline reaction by addition of a stronger acid, or the soaps are used in acid media, the fatty acids are set free as an insoluble, curdy mass and the detergent ability of the soap is destroyed. Furthermore, if ordinary sodium or potassium soaps are used with hard or brackish waters containing calcium and magnesium compounds, these react with the soap to form insoluble, curdy calcium and magnesium soaps which have no detergent value and are extremely difficult to rinse from fabrics. The $-O-SO_2OH$ and $-SO_3H$ groups have much stronger acidic properties than the $-COOH$ group of the fatty acids; consequently, the sodium or potassium salts of sulphated and sulphonated fatty compounds form practically neutral solutions in water, are affected neither by alkalies nor by moderately strong acid media at ordinary temperatures, and moreover may be used with hard or brackish waters since the calcium and magnesium salts formed are appreciably soluble in water, particularly hot water. The $-SO_3H$ group in sulphonated compounds is stable toward even the strongest mineral acids, whereas the $-O-SO_2OH$ group in sulphated compounds is hydrolyzed to $-OH$ by mineral acid solutions on warming. Even when decomposed by acid media, the liberated fatty substances are soluble and have no disadvantageous action (i.e. development of rancidity).

Commercially "sulphonated" oils are liquids varying in colour from light amber to a dark brown; they are heavier than water and give clear or slightly turbid colloidal solutions with water. The solubility depends on the nature and degree of unsaturation of the original oil, and on the degree of sulphation and sulphonation as regulated by the conditions of processing. Little attempt is made commercially to separate individual compounds, and the alkali salts are generally made in solution during use. Hence the complex mixtures met with seldom allow recognition or classification of the individual physical properties of such compounds, some of which probably are solids when pure. The characteristics of some "sulphonated" Canadian fish oils prepared in these laboratories are given in Section 8.

Efforts have been made commercially to produce new soap-like compounds by the extensive sulphation or sulphonation of unsaturated oils, but it has been found that, although the solubility in water of these substances and their metallic salts was excellent, the detergent power was not satisfactory. Therefore they have been adapted to other, equally important, non-detergent uses. Thus, oils

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containing several oleic acid constituents can be highly sulphonated to form products (e.g. "Praestabilol V") that appear to yield a stable chemical union with the basic radicals of wool fibres. The chemically held fat gives the wool a desirable feel, softness and fullness. Fish oils contain the highly unsaturated acids necessary for forming highly sulphated and sulphonated oils, although it is claimed (Winokuti and Toriyama 1936) that, in the processing of some fish oils (herring), the difficulty of preventing decomposition of the first-formed sulphates, even at low temperatures, prevents good sulphated oils being formed from such sources. The hydroxy acids resulting from the decomposition cause a turbidity in the finished product, since they and their salts are only very slightly soluble in water. Some fish and marine mammalian oils are, however, valuable raw materials for the production of suitable sulphated and sulphonated oils. Canadian cod, salmon, whale, sperm, porpoise and grayfish oils are being "sulphonated" and used in the Canadian leather industry. These oils, together with other Canadian fish oils not suitable for direct "sulphonation", are undoubtedly suitable for the production of sulphated or sulphonated individual fatty acids, alcohols, etc., since the individual characteristics of the oil are largely submerged in processing.

The sulphated and sulphonated fatty alcohols and related compounds mentioned under (iii) and (v) above have attained prominence lately because of the accentuated nature of their detergent and wetting powers. They are usually used in the form of their sodium salts (non-crystalline powders or granules). They are extremely surface-active, reduce the surface tension of water, concentrate in a film at the surface when in solution, and reduce the interfacial tension between water and materials not easily wetted by water. These properties account for their powerful wetting-out and penetrating ability, and their strong emulsifying and dispersive action. "Aerosol OT Dry" received considerable publicity as a representative of this class of detergent when it was demonstrated that one part in 2000 of water so wetted the feathers of a duck that the duck could no longer float. It appears to be a generality that the further the sulphur-containing group is from the centre of the fatty portion of the molecule, the greater the detergent power. In the above detergents the group is at or beyond the end of the fatty carbon chain; in sulphated oils and fats the group is usually near the centre of the chain and the detergent power is less, despite the presence of the original soap-forming $-COOH$ group in the case of the sulphated fatty acids.

Technical lauryl sodium sulphate, known as "Gardinol WA" and "Orvis", (actually a mixture of sodium salts of sulphated C_{10} to C_{14} saturated alcohols) and technical sodium oleyl sulphate, known as "Gardinol CA", (unsaturated C_{16} to C_{18}) are important detergent products since solubility, resistance to acids and hard water, wetting-out and emulsifying properties are greatest at C_{12} and gradually decrease to C_{18}, beyond which the sodium salt is too slightly soluble to be of use. Technical sodium stearyl sulphate, known as "Brilliant Avirols", (saturated C_{16} to C_{18}) contains cetyl and some myristyl products and being more fatty in nature than the former products, is not used so much as a detergent as for a softener and finishing agent in the textile industry.

The solubility (colloidal solutions) of the sodium alcohol sulphates in water varies with their chemical structure. The lauryl (C_{12}) salt gives a 20 per cent solution at 15°C., and is sufficiently soluble in ice water to form good suds. The oleyl (C_{18}) salt gives only a 1-2 per cent solution at ordinary temperatures, but a 15 per cent solution at 50°C. The stearyl (C_{18}) salt can be used advantageously only above 50°C. As already stated, metallic alcohol sulphates are more soluble than the corresponding metal soaps. The solubility is roughly analogous to the solubility of the inorganic sulphate of the metal. Thus, the alcohol sulphates of copper

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and magnesium are more soluble than those of sodium, while those of calcium and potassium are less so. Aluminium, iron, lead and tin lauryl sulphates are soluble to a slight extent at 15°C. The rise in solubility with increasing temperature is remarkable. The solubility of calcium lauryl sulphate in water is 0.05 per cent at 53°C., increasing to 0.5 per cent at 54°C.; calcium stearyl sulphate, 0.002 per cent at 93°C., increasing to 0.05 per cent at 95°C. The calcium and other salts are much more soluble in the presence of the sodium salt, probably due to a protective colloidal action. A contrast between the sulphate and sulphonate of one given fatty compound is that the calcium salt of the former is more soluble in water than that of the latter; the solubilities of the sodium, calcium and magnesium salts of sulphonated fatty alcohols from C_8 to C_{18} have been fully investigated and shown to be less than formerly supposed (Reed and Tartar 1936; Tartar and Wright 1939).

In summarizing, sulphated and sulphonated oils and fatty acids find their principal applications in the textile, leather and soap industries, where respectively they serve as: wetting-out agents, softeners, "assists" in printing (of textiles), conditioners of textile threads, general emulsifiers and detergents; fat liquor ingredients in finishing of leather and de-hairing agents (for hides); ingredients of shampoo and shaving preparations. They also find application as disinfectants and spreading agents for spraying compounds, bodiers of perfumes, ore-flotation agents, ingredients of certain printing inks, retainers of flexibility in glue and adhesive-coated papers, and in many other fields. Sulphated and sulphonated fatty alcohols are used to an increasingly greater extent in many industries. Their stability and great emulsifying powers particularly suit them for such uses as: wetting, cleansing and finishing agents in textile manufacture and in the dyeing and printing of textiles; assists in the chrome liquoring and finishing of leathers; bases for cosmetics and toilet preparations. A recent example of their emulsifying ability is to be found in their use as a paste softener in removing old wallpaper.

(g) SULPHURIZATION

Sulphurization is the process of bringing sulphur into direct chemical combination with the carbon atom chain of fatty substances, and was patented as early as 1846 for the purpose of manufacturing from oils "articles having purposes analogous to gutta percha".

The two underlying processes of sulphurization are: (1) heating fatty oils or fatty acids with powdered elemental sulphur (S), whereby a gradual increase in viscosity and darkening of colour takes place with eventual formation of a gel, rubbery material or solid, commonly termed "brown" or "black" *factice*; (2) reaction of oils or fatty acids with liquid or vaporized sulphur monochloride (S_2Cl_2) at ordinary temperatures, whereby similar changes take place with less darkening of colour. The reaction is exothermic and requires careful control to prevent the temperature from becoming too high. The products so obtained are commonly referred to as "light" factice.
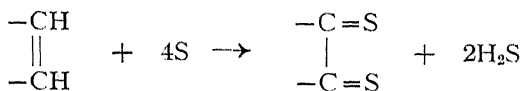
Factices are used as fillers in rubber compounding, as rubber substitutes, as ingredients in the manufacture of paints, varnishes, linoleum, ore-flotation compounds, insecticides, and in the leather and other industries. Further details of the actual processes and products will be found in Section 8 II (*f*).

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Reaction between sulphur and *saturated* fatty oils or acids may result in alteration of the physical properties of the oil or acid, but little if any chemical combination appears to take place; the process is mainly one of polymerization through the agency of the heat applied and of a possible promoting or catalytic effect of the sulphur. With *unsaturated* oils or acids, actual chemical addition of sulphur to the double bonds takes place, and as sulphur has certain chemical properties analogous to those of oxygen, the reaction is of the same complex nature as described under oxidation and polymerization, except that sulphur takes the place of oxygen to form such complexes as:

$$
\begin{array}{c}
-\mathrm{HC} \\
\| \\
-\mathrm{HC}
\end{array}
+ \text{ sulphur } \longrightarrow
\begin{array}{c}
-\mathrm{HC} \\
| \\
-\mathrm{HC}
\end{array}\!\!\!\Big\rangle\mathrm{S},
\quad
\begin{array}{c}
-\mathrm{HC-S} \\
| \quad | \\
-\mathrm{HC-S}
\end{array},
\quad
\begin{array}{c}
-\mathrm{HC-S-S-CH-} \\
| \qquad\quad | \\
-\mathrm{HC-S-S-CH-}
\end{array}, \text{ etc.}
$$

Double bond   Non-polymerized   First stage in formation
                       sulphurized products   of polymerized products.
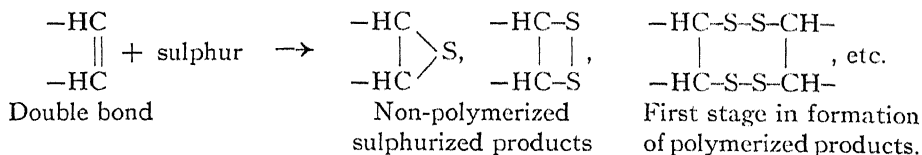
Little or no sulphur separates out on cooling the reaction product, only traces of hydrogen sulphide (H_2S) are set free, and on hydrolyzing a sulphurized fat, the liberated fatty acids are still sulphurized. The almost complete lack of hydrogen sulphide formation in either the sulphurizing process or subsequent hydrolysis indicates that little if any substitution of hydrogen by sulphur has taken place:

$$
\begin{array}{c}
-\mathrm{CH} \\
\| \\
-\mathrm{CH}
\end{array}
+ \ 4\mathrm{S} \ \longrightarrow
\begin{array}{c}
-\mathrm{C}=\mathrm{S} \\
| \\
-\mathrm{C}=\mathrm{S}
\end{array}
+ \ 2\mathrm{H}_2\mathrm{S}
$$

If sulphurized fatty acids are heated to a sufficiently high temperature (180° to 200°C.), further reactions occur with evolution of hydrogen sulphide.

(ii) WITH SULPHUR MONOCHLORIDE

Sulphur monochloride can react with both saturated and unsaturated fats and fatty acids. With the *saturated* compounds the process is relatively slow and not very energetic; it appears to be mainly one of substitution with splitting off of gaseous hydrogen chloride:

$$
\begin{array}{c}
| \\
\mathrm{HCH} \\
|
\end{array}
\quad + \quad
\mathrm{Cl-S-S-Cl} \ \longrightarrow
\begin{array}{c}
| \\
\mathrm{HC-S-S-Cl} \\
|
\end{array}
\quad + \quad
\mathrm{HCl}
$$

Link in carbon   Sulphur   Sulpho-   Hydrogen
   atom chain   monochloride   chlorinated   chloride
                                 compound
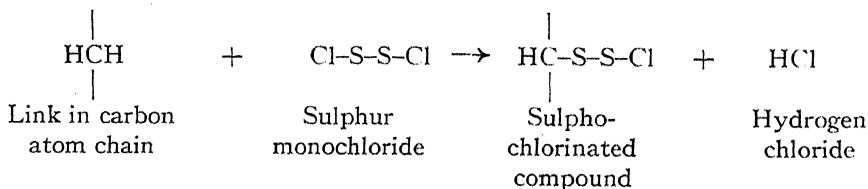
followed by a further reaction with a second fatty carbon atom either in the same molecule, or in another molecule with formation of a dimer:

$$
\begin{array}{c}
| \\
\mathrm{CH-S-S-Cl} \\
|
\end{array}
\quad + \quad
\begin{array}{c}
| \\
\mathrm{H}_2\mathrm{C} \\
|
\end{array}
\quad \longrightarrow \quad
\begin{array}{c}
| \qquad\quad | \\
\mathrm{CH-S-S-HC} \\
| \qquad\quad |
\end{array}
\quad + \quad
\mathrm{HCl}
$$

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Such reactions can continue among the fatty molecules to form trimers and polymers. In the case of the *unsaturated* fats and fatty acids, the reaction is rapid and energetic and may become violent if not controlled by cooling or presence of an inert solvent. The first step is undoubtedly one of direct addition of sulphur to the double bond:

$$
\begin{array}{ccccc}
-\text{HC} & & \text{S--Cl} & & -\text{HC--S--Cl} \\
\parallel & + & \mid & \rightarrow & \mid \\
-\text{HC} & & \text{S--Cl} & & -\text{HC--S--Cl}
\end{array}
\qquad \text{(no HCl liberated)}
$$

<div align="center">

Double   Sulphur   Sulphochlorinated
bond   monochloride   compound

</div>
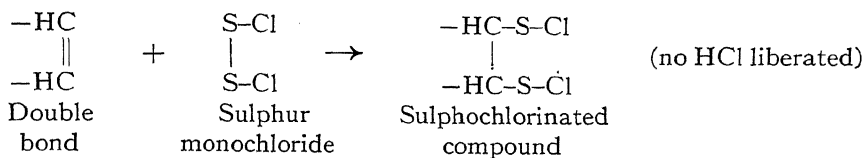
Some substitution as indicated in previous formulae appears to take place simultaneously though more slowly, as evidenced by liberation of some hydrogen chloride. The further steps in the reaction are not fully understood but can consist of further substitution either in the same or adjoining molecules:

$$
\begin{array}{ccccc}
-\text{HC--S--Cl} & & \text{HCH--} & & -\text{HC--S--CH--} \\
\mid & + & \mid & \rightarrow & \mid\quad\mid \qquad + \ 2\text{HCl} \\
-\text{HC--S--Cl} & & \text{HCH--} & & -\text{HC--S--CH--}
\end{array}
$$
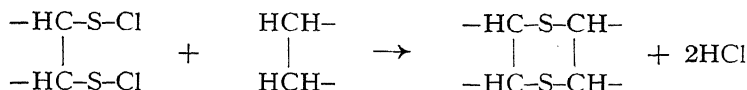
and formation of other linkages wherein sulphur, chlorine, or both are combined in various ways with the carbon atoms of single molecules and polymerized products.

Both of the above methods of sulphurization may lead to a partial splitting of fatty acids from the glycerine portion of fats, with subsequent action of the reagents on the fragments of the molecule.

In the action of sulphur monochloride on unsaturated oils, investigation has shown (Kaufmann, Baltes and Mardner 1937) that the actual decrease in the iodine value of the original oil is much greater than would be expected from the amount of sulphur monochloride combined. This gave evidence for the view that intra-molecular and polymerizing reactions among the double bonds play a considerable part in the process. Diagrams of the amount of monochloride taken up at the end of various reaction intervals showed various "halts" in the reaction curve which indicated different stages such as initial addition of reagent, formation of dimers and polymers, and splitting off of hydrogen chloride. The rapidity, energy, and total amount of sulphurization with sulphur monochloride appeared to bear no direct relation to the amount of unsaturation in the oil. For example, after complete reaction with a cod liver oil and a more unsaturated linseed oil, the ratio of the amounts of monochloride combined was $\dfrac{\text{cod liver oil}}{\text{linseed oil}} = 0.85$ whereas the ratio of the iodine values (unsaturation) of the original oils was 0.65. Thus the less unsaturated cod liver oil combined with the greater amount of reagent. This appears to hold true generally in the sulphurization of unsaturated marine animal oils as compared with similarly unsaturated vegetable oils. The fish oils in reacting with sulphur monochloride cause the evolution of much more hydrogen chloride than do the vegetable oils, which leads to a preponderance of sulphur

<div align="center">143</div>

over chlorine in the final factice from fish oils. Whether this preponderance is detrimental is open to question, but the considerable evolution of hydrogen chloride is detrimental for some purposes.

Several modifications of the basic reactions noted above are employed in industrial sulphurization, but, since in many instances the details are trade secrets not fully disclosed in the patents, several of these modifications will be described briefly here instead of being treated under "Processing" in Section 8 II(f).

Oils are frequently "blown" to partially oxidize them either before, during or after the sulphurizing process. Cobalt and manganese driers may be added during the blowing (Heublyum 1935). Whereas a raw unsaturated oil may require 20 to 25 per cent of its weight of sulphur monochloride to get a desired product, the same oil after being thoroughly blown may require as little as one per cent. The necessary degree of blowing depends on the properties desired in the technical product, usually a varnish. If the blowing is carried too far, the oil cannot combine with sufficient sulphur to attain any significant further changes in properties. By using insufficient sulphur or monochloride for complete reaction with raw or blown fish oil (Pawelzik 1939), liquid "semi-factices" are obtained which have accentuated drying powers and other properties desired for paints and varnishes, as compared with the drying powers of the original oils or the normal factices prepared from them. Several patents deal with other types of preliminary treatments, such as French patent 672,503 describing emulsification of the oil, and American patent 1,957,437 describing the heating of fish oils to 200° to 300°C. with water-free alkalies followed by cooling and sulphurizing with sulphur to yield a solid vulcanized product.

Distinct from the above pre-treatment of oils is the action of sulphurizing agents on oils and fatty acids that have undergone definite chemical processes such as halogenation or esterification. British patent 284,415 describes the vulcanization of chlorinated, formylated and acetylated unsaturated fatty acids by means of sulphur monochloride, etc.; British patent 340,012 states that chlorinated saturated and unsaturated fatty acids may be sulphurized with alkali sulphides (see below) in such a way as to yield a preponderance of $-CH(SH)-$ plus $-CH(OH)-$ groups instead of the sulphurized groups already formulated.

Finally, the action of other sulphurizing agents may be mentioned. Hydrogen sulphide in the presence of "carriers" has recently been employed for the production of a superior, chlorine-free white factice. Dithiocyanogen [$(SCN)_2$] and the closely related thiocyanates (KSCN), sulphides and polysulphides of calcium (CaS_x) and sodium (Na_2S), organic sulphides produced from ethylene dichloride, and others have been investigated (British patents 284,415; 340,012; 313,917). Selenium, an element resembling sulphur, also forms a chloride (Se_2Cl_2) whose "selenizing" action on whale, menhaden, and cod liver oils and oleic acid has been studied (Harvey and Schuette 1928). Judged by the rapidity of the rise in temperature produced, selenium chloride reacts more energetically than the sulphur chloride also tested on the same oils but no particularly useful products were indicated. The action of the element selenium on stearic acid has been investigated (Bertram 1936) and shown to result in the formation of saturated and unsaturated hydrocarbons.

(h) HYDROXYLATION

Hydroxylated fatty compounds contain one or more hydroxy groups attached to intermediate carbon atoms of a fatty carbon chain. Fats containing naturally-occurring hydroxylated fatty acid constituents are found in appreciable quantities

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only in certain vegetable oils such as castor oil. To produce hydroxylated fats, fatty acids, or other fatty compounds from marine animal sources therefore requires introduction of the hydroxyl group by some process of *hydroxylation*.

The introduction of hydroxyl groups into a fat or fatty acid raises its melting and boiling points, increases its solubility in certain solvents such as alcohol, and renders it somewhat soluble in hot water or even cold water if sufficient hydroxyl groups have been introduced. An increase in the viscosity is also experienced, and this property, together with the "oiliness" and other factors desirable in lubrication (page 360), has led to investigations of artifically hydroxylated oils to determine their suitability as lubricants in view of the success of refined castor oil as a lubricant for aeroplane motors.

Saturated fats and fatty acids may be made to undergo hydroxylation by a process of halogenation and replacement of the halogens by hydroxyl groups, but unsaturated fats and fatty acids are better adapted as starting materials and only such will be considered here. The following reactions are exemplified by fatty acids, although it is to be understood that in most cases the unsaturated fatty acid constituents of fats behave analogously.

(i) THROUGH SULPHATION

It has been indicated on page 135 how sulphation can lead to the introduction of one hydroxyl group per double bond of an unsaturated fatty acid. American patent 722,129 granted in 1904 describes such a process for producing from oleic acid, in yields of 85 to 90 per cent, a candle-making material consisting chiefly of a monohydroxy stearic acid:

$CH_3.(CH_2)_7.CH = CH.(CH_2)_7.COOH$ Oleic acid

$\downarrow$ Action of sulphuric acid

$CH_3.(CH_2)_7.CH–CH_2.(CH_2)_7.COOH$ $\qquad$ $CH_3.(CH_2)_7.CH–CH_2.(CH_2)_7COOH$

$\qquad$ | $\qquad\qquad\qquad\qquad\qquad\longrightarrow\qquad$ |

$\qquad$ O.SO_2.OH $\qquad$ Hydrolysis $\qquad$ OH

$\qquad$ Sulphated oleic acid $\qquad\qquad\qquad$ 10-hydroxy stearic acid
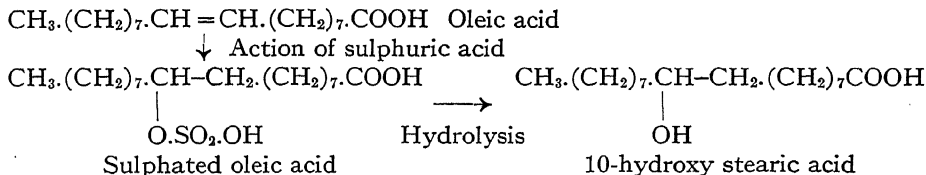
This same process forms the basis of English patent 388,630 (1933) whereby various whale oils are mixed with concentrated sulphuric acid at low temperatures, allowed to stand, then mixed with an excess of water and heated with direct steam. The hydroxylated products are stated to be miscible with water, fatty and mineral oils and to be useful in the leather industry as substitutes for degras.

(ii) THROUGH HALOGENATION

Two basic methods are available, both of which are included in an American patent (901,905) issued to G. Imbert in 1908 and introduce *two* hydroxyl groups per original double bond. The first method consists in treating the unsaturated acid (oleic) with chlorine to form dichlorostearic acid. Ten parts by weight of this acid are then mixed with 3.5 parts of caustic soda and 50 parts of water and heated under pressure for 3 hours at 120°C. The dihydroxy stearic acid is precipitated out by the addition of acid.

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$$R.CH = CH.R' \xrightarrow{Cl_2} \begin{array}{c} R.CH-CH.R' \\ | \quad | \\ Cl \quad Cl \end{array} \xrightarrow{2NaOH} \begin{array}{c} R.CH-CH.R' \\ | \quad | \\ OH \quad OH \end{array} + 2NaCl$$

Unsaturated fatty acid	Dichloro fatty acid	Dihydroxy fatty acid
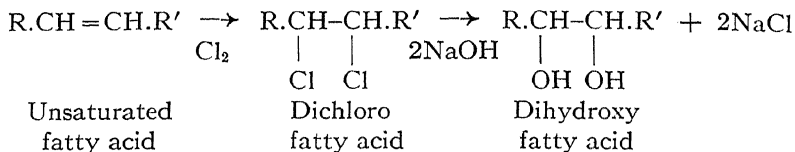
English patent 340,011 (1929) covers a similar process, whereby halogenated fatty acids containing more than eight carbon atoms are converted into partially or fully hydroxylated fatty acids whose alkali salts are suitable cleansing and emulsifying agents.

The second process consists in saturating the double bond with hypochlorous acid (HOCl) formed *in situ* by the simultaneous action of chlorine and an aqueous solution of sodium carbonate on the unsaturated acid:

$$R.CH = CH.(CH_2)_n.COOH + Cl_2 + Na_2CO_3$$
$$\begin{array}{c} R.CH-CH.(CH_2)_n.COONa + NaCl + CO_2 \\ | \quad | \\ Cl \quad OH \end{array}$$
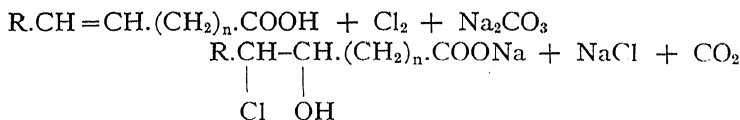
The resulting chlorohydroxy fatty acid is converted into the dihydroxy fatty acid by the excess of sodium carbonate by raising the temperature (under pressure) to 150°C. for 6 hours. It was claimed that this process may be employed for hydroxylating various unsaturated acids and oils such as cod liver oil. The amounts of reagents are governed by the degree of unsaturation as indicated by the iodine value of the original material. A somewhat similar process patented in 1936 (American patent 2,033,538) describes the treatment of sodium oleate with sodium hypochlorite (NaOCl) in the presence of a hypochlorite-decomposing reagent serving to liberate oxygen, such as nickel oxide. The product is dihydroxy stearic acid.

The halogenation of double bonds by hydrogen chloride, bromide or iodide (page 148) provides intermediate compounds from which hydroxylated acids containing *one* hydroxyl group per original double bond may be formed (X = Cl, Br or I):

$$\begin{array}{c} \nearrow R.CH = CH.R' + HX \\ R.CH-CH_2.R' \\ \searrow R.CH-CH_2.R' \\ X OH \end{array}$$
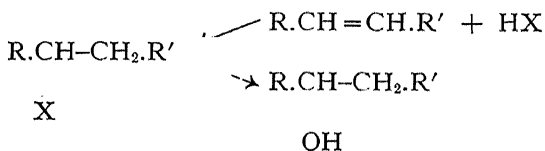
(iii) THROUGH PARTIAL OXIDATION

Several methods are available, of which some, although they produce high yields of fully hydroxylated fatty acids, are hardly practicable from a technical standpoint because of their unwieldiness (e.g. partial oxidation with alkaline solutions of potassium permanganate, Nunn and Smedley-MacLean 1938) or because of the expensive nature of the necessary reagents (partial oxidation with hydrogen peroxide in solutions of tertiary butyl alcohol, using osmium tetroxide

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as catalyst, Milas, Sussman and Mason 1939). More direct methods, possibly capable of technical development in connection with fish oils and fatty acids, consist of (1) passing hydrogen containing oxygen into the unsaturated material at a temperature of about 255°C. in the presence of one per cent finely divided nickel oxide catalyst (American patent 1,026,339), whereby monohydroxy stearic and stearic acids are produced from oleic acid; (2) continued oxidation of unsaturated fatty acids by passing atmospheric oxygen into the material at 120°C. for 18 hours in the presence of a catalyst such as the manganese salt of a fatty acid (Davankov and Fedotova 1936). Almost complete conversion into hydroxy acids with formation of only traces of volatile acids is stated to result.

In some experiments carried out in these laboratories (Tipson unpub.) attempts were made to produce hydroxylated grayfish liver oil by hydroxylation through halogenation and partial oxidation. The action of hydrogen bromide gave a completely hydrobrominated oil of reproducible properties, but satisfactory removal of the bromine could not be effected. Treatment of the liver oil with a mixture of three volumes of hydrogen and one of oxygen under atmospheric pressure at temperatures up to 180°C. in the presence of nickel oxide catalyst caused some hydroxylation as indicated by a 26 per cent rise in viscosity and increase of acetyl value from 5.68 to 11.05. How much of this may have been due to hydroxylation of unsaponifiables was not determined. It is suggested that similar treatment conducted under pressure at an elevated temperature (225°C.) might be more efficacious.

The number of possible hydroxylated derivatives obtainable from one carbon atom chain containing several double bonds is very great. Depending on the number of hydroxyl groups introduced, several derivatives of different composition will be formed, and each of these may be produced in many isomeric forms depending on the position of the hydroxyl groups in the chain and the spatial isomerism of these groups. A description of several of the better characterized hydroxy acids obtainable from unsaturated fatty acids commonly found as constituents of marine animal oils follows.

Normal oleic acid (melting point 16°C.) can yield two monohydroxy stearic acids, $CH_3.(CH_2)_7.CH(OH).CH_2.(CH_2)_7.COOH$ and $CH_3.(CH_2)_7.CH_2.CH(OH).(CH_2)_7.COOH$, of which the former is the more common and melts at 81.5°C. Fully hydroxylated normal oleic acid, $CH_3.(CH_2)_7CH(OH).CH(OH).(CH_2)_7.COOH$ or dihydroxy stearic acid, melts at 132°C. and is insoluble in hot or cold water. A geometrical isomer melting at 95°C. is formed by hydroxylation of elaidic acid. Several other isomers obtainable from iso-oleic acids are also known.

Normal linoleic acid (melting point −8°C.) yields at least four isomeric tetrahydroxy stearic acids (sativic acids) having the same formula:
$CH_3.(CH_2)_4.CH(OH).CH(OH).CH_2.CH(OH).CH(OH).(CH_2)_7.COOH$ and melting points of about 122°, 146°, 160° and 174°C. These sativic acids are insoluble in cold water, but slightly soluble in hot water. Two other isomeric sativic acids of the above constitution may be obtained by hydroxylation of elaidinized linoleic acid.

Normal linolenic acid (liquid at room temperature) is capable of yielding many isomeric hexahydroxy stearic acids (linusic acids) of the formula:
$CH_3.CH_2.CH(OH).CH(OH).CH_2.CH(OH).CH(OH).CH_2.CH(OH).CH(OH).(CH_2)_7.COOH$
of which two, melting at about 174° and 196°C., have been definitely studied. These two linusic acids are slightly soluble in cold water and readily soluble in hot water.

A hydroxy acid containing eight hydroxyl groups, melting point 195°C. and readily soluble in hot and cold water, is described as being formed from arachidonic acid.

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Only those derivatives containing one or two hydroxyl groups per carbon atom chain could be considered as useful in the field of lubrication; those with three or more hydroxyl groups may find application in the detergent field after esterification with solubilizing groups, but the ordinary alkali salts do not form useful soaps (Dieterle 1939).

(*i*) HALOGENATION.

The addition of halogens at the double bond in fatty acids has already been discussed in Section 2 of this Bulletin. When oils are treated with halogens the actual addition takes place in much the same way as in the free fatty acids, but, as might be expected, the properties of the addition compounds are different from those obtained with the acids. If chlorine gas is passed into a fish oil, considerable darkening takes place and the oil becomes thicker in consistency. At room temperature quantities of hydrogen chloride are evolved, indicating that substitution by chlorine, as well as addition, is taking place. The action of bromine depends on the manner in which it is allowed to act on the oil, that is, on whether it acts as a dry vapour, as a liquid or when dissolved in one of the many available solvents. Thin films of fresh oil exposed to dry vapour in the dark absorb bromine by addition at the double bonds, no substitution taking place. Bromine liquid, added to oils in bulk or in solvents, causes substitution unless the reaction mixture is kept cold. With fish oils the addition of bromine produces a precipitate of brominated glycerides due to the formation of octa- and deca-bromides of the highly unsaturated fatty acids present in these oils. Solutions of bromine in various solvents are used for analytical purposes to estimate the amount of unsaturation of an oil. If the oil is fresh, these solutions usually do not cause substitution, but oxidized or polymerized oils are immediately substituted even by bromine vapour or mild brominating reagents such as pyridine sulphate dibromide. Iodine from solution in alcohol, chloroform, etc., is absorbed slowly by oils and usually complete addition is never attained. Substitution does not take place with this halogen.

Compounds of iodine with bromine or chlorine add quantitatively at the double bonds of the fatty acids of oils and are used extensively to determine the unsaturation of such materials. Iodine monochloride and monobromide are two of the more common halogenating reagents. Dissolved in glacial acetic acid or in neutral solvents such as carbon tetrachloride, these compounds do not give substitution when used on fresh oils, but in the presence of oxidized or polymerized oils substitution is extensive. With fish oils both these reagents give copious precipitates due to the formation of insoluble iodochlorides or iodobromides of the highly unsaturated fatty acids.

The addition of hydrogen bromide and hydrogen chloride to fish oils has been investigated in these laboratories by Tipson (unpub.). Dry hydrogen bromide gas was absorbed quantitatively by dogfish liver oil. The product was a clear, very viscous, pale yellow oil that possessed a faint sweet smell quite unlike that of the odour of the original oil. It gave no precipitate on standing overnight

in a refrigerator. The hydrobrominated oil contained 26.2 per cent bromine and had a viscosity of 1.446 poises at 40°C. as contrasted with 0.325 poises for the original oil. Dry hydrogen chloride is not absorbed by the double bonds in unsaturated oils. Passage of hydrogen chloride through dogfish liver oil resulted in a small absorption (1.35 per cent) of chlorine that later was found to be combined with the unsaponifiable matter present in the oil.

Halogenated vegetable oils are used in X-ray examinations of various body cavities since these substances are more or less opaque to the rays. Iodized olive, sesame and cottonseed oils are most generally used, it being stated that halogenated cod liver oils are unstable and undergo rapid hydrolysis with consequent irritation at the locality of the injection. Various means of stabilizing halogenated oils have been suggested. According to Greenbaum (1937) oils containing both chlorine and iodine are more stable than those containing iodine alone and he suggests the use of iodine monochloride as a suitable halogenating reagent. Although iodized oils have been used to the greatest extent in roentgenology, recent work indicates that brominated oils possess definite advantages over the iodized. Tabern, Hansen, Volwiler and Crandall (1930) found that brominated olive oil and olive oil esters are much more stable and cause less irritation than iodized oils. Since the opacity of a halogenated oil to X-rays depends upon the nature and amount of halogen present, it is possible that the more highly unsaturated fish and fish liver oils could be used for this purpose provided that the product was liquid and thoroughly stable.

Halogenated fish oils have from time to time been suggested for various industrial purposes. British patent 323,801 describes the manufacture of a highly chlorinated fish oil which has good adhesive and weather-resisting properties when used in paints. Chlorine is passed into the oil at temperatures between 40° and 50°C. until no more is absorbed. Air or an inert gas is then passed through the oil for several hours at 70°C., followed by air containing a small amount of ammonia. Finally a small amount of monoethylaniline is added as a stabilizer. Hirose and Shimomura (1929) endeavoured to deodorize herring oil for soap manufacturing purposes by passing chlorine through it at 18° to 20°C. Much substitution took place and the soap manufactured from the treated oil became dark and gave off an irritating odour. According to French patent 755,486 chlorinated oils and fatty acids can be stabilized by the addition of derivatives of ethylene oxide such as epichlorohydrin, phenoxypropene oxide or dimethylglycidol. A resinous product suitable for coating cloth, paper, etc., is manufactured, according to United States patent 2,044,007 by chlorinating an oxidized drying oil such as linseed oil, then heating at 77° to 95°C. until all the chlorine is driven off. A somewhat similar process is described by Gardner and Bielouss (1922), who chlorinated and dechlorinated such semi-drying oils as soy bean and cottonseed oils. It is claimed that such a treatment greatly improved the drying properties of these oils.

(j) ELAÏDINIZATION.

Elaidinization is the spatial rearrangement of two different chemical groups attached to one carbon atom of a double bond in an unsaturated fatty molecule. The geometrically isomeric substance thereby formed has the same chemical composition as the original material, but exhibits new chemical and physical properties. This reaction was recognized as early as 1819 when it was observed

that "brown nitrous fumes" (a mixture of oxides of nitrogen) caused a partial solidification of certain liquid vegetable oils. The double bond affected is usually that of a fatty acid carbon chain, either esterified in the form of a fat, or as the free acid, as exemplified by the elaidinization of oleic acid into elaidic acid:

$$
\begin{array}{ccc}
\begin{array}{l}
CH_3.(CH_2)_6.CH_2\text{--}C\text{--}H \\
\qquad\qquad\qquad || \\
COOH.(CH_2)_6.CH_2\text{--}C\text{--}H
\end{array}
& \rightleftharpoons &
\begin{array}{l}
CH_3.(CH_2)_6.CH_2\text{--}C\text{--}H \\
\qquad\qquad\qquad\qquad || \\
\qquad\qquad H\text{--}C\text{--}CH_2.(CH_2)_6.COOH
\end{array}
\end{array}
$$

Oleic acid ($C_{18}H_{34}O_2$), melting   Elaidic acid ($C_{18}H_{34}O_2$), melting
    point 16°C. (cis-isomer)   point 44.5°C. (trans-isomer)
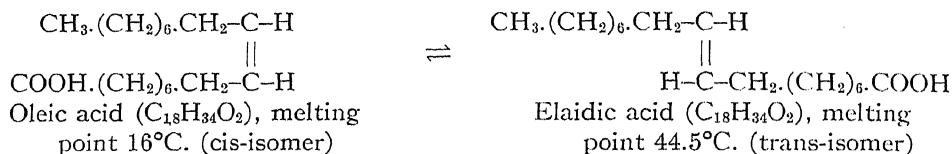
As indicated by the double arrow, the reaction is reversible. An equilibrium mixture of the original substance and its elaidinized isomer is obtained, in which the proportion of the two isomers present depends on the nature of the original material and the efficiency of the elaidinizing reagent. In the case of oleic acid and several other unsaturated acids equilibrium is reached when about two-thirds of the original substance has been elaidinized; if the pure elaidinized product is isolated from this mixture and again subjected to the action of the elaidinizing reagent, one-third of it is transformed back into the original substance to give the same equilibrium mixture as before. If glycerol tri-oleate (olein) is elaidinized, equilibrium is established when two-thirds of the oleic acid radicals has been converted into elaidic acid radicals, but the equilibrium mixture contains only about 30 per cent of glycerol tri-elaidate; the remainder consists of unchanged tri-oleate together with mixed oleic-elaidic glycerides.

Elaidinized fats have never yet been found in natural products although it has been shown that they are readily assimilated and incorporated into the body fat when fed to animals.

For industrial purposes, elaidinization is useful for raising the melting point of unsaturated fats and fatty acids that are either liquid or too soft at ordinary temperatures, without resorting to hydrogenation which would partially or completely remove the unsaturation characteristics whose retention may be desired (American patent 2,165,530; 1939). The melting point of the equilibrium mixture of the original substance and its elaidinized isomer as a rule lies between the melting points of the isomers, due to the "lowering of the melting point" effect (page 158). Thus the equilibrium mixture containing about 33 per cent of the oleic acid and 67 per cent of elaidic acid melts at about 38°C., much closer to the melting point of elaidic acid (44.5°C.) than to that of pure oleic acid (16°C.). Actually, commercial oleic acid is usually liquid at temperatures appreciably below 16°C. because of the lowering of melting point caused by small amounts of dissolved impurities.

The rise in melting point by elaidinization allows the use of soft fats in candle manufacture and in the preparation of soaps. Recent investigations (Bertram and Kipperman 1936) indicate that soaps from elaidinized fatty acids have cleansing powers superior to those from the untreated acids, as judged by washing tests, wetting and emulsifying power, and formation and stability of suds.

Mono-unsaturated fatty acids that occur in marine animal oils and are capable of undergoing elaidinization are, in addition to oleic acid (C_{18}), lauroleic (C_{12}), myristoleic (C_{14}), palmitoleic(C_{16}), eicosenoic (C_{20}), cetoleic (C_{22}) and selacholeic (C_{24}) acids. Naturally-occurring (cis-) selacholeic acid melts at 42°C., while the elaidinized acid (trans-isomer) melts at 61°C. Glycerol tri-oleate (olein) melts at about 6°C.; the isomeric tri-elaidate (elaidin) melts at 40.5°C. Fatty substances containing more than one double bond in the carbon atom chain can also undergo elaidinization. Thus the di-unsaturated linoleic acid (melting point −8°C.) occurring as a major constituent in vegetable oils can exist in four geometrically isomeric forms, only two of which (one melting at 29°C. and the other a liquid at ordinary temperatures) appear to be formed during elaidinization (Kass and Burr 1939). The equilibrium mixture is soft at room temperatures due to the "lowering of the melting point" effect.

Partly oxidized fatty acids, or even unsaturated acids in the incipient stages of oxidation through appreciable exposure to air, do not elaidinize as completely as freshly prepared or recently distilled acids.

Elaidinizing reagents act catalytically inasmuch as very small amounts are capable of transforming large quantities of unsaturated fatty substances. A common method consists of floating the liquid or melted fatty substance on a 70 per cent aqueous solution (spec. grav. 1.42) of nitric acid acting on mercury or arsenic trioxide at a temperature between 10° and 20°C. The oxides of nitrogen liberated from the acid rapidly elaidinize the fatty layer while bubbling through it. The progress of the reaction is controlled by observing the increase in melting point of samples withdrawn from time to time, and on completion of the process the warm elaidinized material is washed free of acid with water. Prolonged action or elevated temperature causes the formation of by-products consisting of stable addition compounds of the fatty substance and the nitrogen oxides. Copper may be used with the nitric acid, but lowers the percentage of elaidinized products from about 66 per cent to only 25 per cent. Oleic acid is 66 per cent elaidinized by agitation with cold 50 per cent sulphuric acid to which is slowly added a cold aqueous solution of sodium nitrite.

A modern method yielding equilibrium mixtures containing maximal amounts of elaidinized product consists in heating fatty substances with one per cent of sulphur or selenium to about 215°C. for 6 hours. The same effect is produced by the action of 0.5 per cent of selenium at 150°C. for 28 hours (Bertram 1938, and German patent 674,752; 1939). Equal amounts of oleic acid and water, heated under pressure to 220°C. with 3 per cent of red phosphorus, yield a snow-white elaidinized product as a result of the bleaching action of certain phosphorus compounds that are formed (Rankov 1936).

During the commercial hydrogenation of unsaturated fats and fatty acids a partial elaidinization contributing to the increase in melting point ("hardening") is said to take place (Moore 1919; Bauer and Herzog 1939).

(*a*) SPECIFIC GRAVITY AND DENSITY.

A practical definition of specific gravity is:

$$\frac{\text{Weight of a given volume of substance at temperature } t°}{\text{Weight of the } same \text{ volume of } water \text{ at temperature } T°}$$

$$= \text{specific gravity of the substance at } \overset{t°}{\underset{\perp}{}}$$

In the marine animal oil industry, T is almost invariably assumed to be 60° F. (15.56° C.) and t is the temperature at which the specific gravity of the oil is measured or stated. Since oils and solid fats expand on warming and contract on cooling, it is evident that with a fixed value for T the specific gravity of an oil decreases with increase in temperature and *vice versa*. Consequently the stating of a specific gravity for an oil without giving the corresponding temperature t is practically meaningless.

If it is desired to compare the specific gravities of different oils when these specific gravities are expressed at different temperatures, a fair comparison can be made only after calculation of the specific gravities at some common temperature t which is frequently chosen as 60° F. to correspond with T in the above definition.

Density is a direct expression of weight per unit volume of a substance, and for liquids it varies appreciably with changes in temperature. Numerical values for densities of liquids are conventionally in terms of grams per cubic centimetre or the almost identical expression, grams per millilitre (1 c.c. = 0.99997 ml.). The following numerical relations are useful in converting values as read on a density or specific gravity hydrometer:

Pounds per Imperial gal. at $t°$ F. = 10.022 ×density (gm./ml.) at $t°$ F.
Pounds per American gal. at $t°$ F. = 8.3454 ×density (gm./ml.) at $t°$ F.
Pounds per cubic foot at $t°$ F. = 62.430 ×density (gm./c.c.) at $t°$ F.

Density (gm./ml.) at $t°$ F. = 0.99904×specific gravity at $\dfrac{t° \text{ F.}}{60° \text{ F.}}$

(1 Imperial gallon = 1.20094 American gallons)

Readings obtained by the use of other types of hydrometers such as the Baumé (of two kinds, depending on whether the liquid is heavier or lighter than water) are best converted to specific gravities or densities by reference to tables.

Actual determination of the specific gravity of a fat is most easily made when the fat is liquid. To find the specific gravity (or density) at a temperature other

than that at which the determination was made, the relation given on page 154 may be employed if the coefficient of cubic expansion of the liquid fat is known. If the new temperature is lower than the one employed, the possibility of the oil being not entirely liquid at the lower temperature must be taken into account, for unlike water, oils contract sharply on solidifying with the result that the solid or semi-solid fat (stearine) has a specific gravity quite appreciably higher than that of the oil. Some pure fatty compounds exhibit a contraction (i.e. specific gravity increase) of as much as 14 per cent when changing from liquid to solid at their freezing point; solid stearic acid and water have the same specific gravity at 52° F. Determinations made on British Columbia pilchard and herring oils in these laboratories (Carter 1937, 1938) have shown that any one sample of either of these oils may have appreciably different specific gravities at a given temperature near the solidifying point depending upon its previous thermal history:

	Spec. grav.
Pilchard oil at 50° F., still liquid after cooling to 50° F.	0.9345
Same oil at 50° F., semi-solid after warming to 50° F.	0.9380
Herring oil at 60° F., still liquid after cooling to 60° F.	0.9235
Same oil at 60° F., semi-solid after standing for 24 hr. at 60° F.	0.9272
Same oil at 60° F., still solid after warming to 60° F.	0.9295

Transactions in marine oils are generally based on weight measurements; and in the case of a bulk quantity too large to be conveniently weighed, the weight is usually calculated from the volume and some form of expression of the specific gravity at 60° F. since weight = volume × specific gravity. It will be evident from the foregoing figures for specific gravity that at a constant temperature near the point of stearine separation the weight of a given volume of oil (or conversely, the volume of a given weight of oil) may vary as much as 0.5 per cent depending on how much stearine is present, which in turn depends on the previous temperature history of the oil. Various considerations in determining and applying such data are discussed in the two reports just mentioned.

The specific gravities of different marine animal oils and liquid products derivable therefrom display wide ranges, while narrower ranges are encountered in different samples of one kind of oil. Examples will be found elsewhere in this Bulletin where individual substances are described. An indication of some ranges encountered follows:

Fish body oils	0.920 to 0.935 at 60° F. (15.56° C.)
Fish liver oils	0.915 to 0.935 at 60° F.
Marine mammal oils	0.910 to 0.930 at 60° F.
Sperm oil	0.875 to 0.885 at 60° F.
Spermaceti (cetyl myristate)	0.832 at 122° F. (60° C.)

Increasing length of carbon atom chain in fatty acids and their glycerides (fats) slightly decreases the specific gravity; increasing unsaturation in a carbon atom

chain of given length appreciably increases the specific gravity; increasing length of chain in fatty alcohols slightly increases the specific gravity, which is much lower than that of the corresponding fatty acid.

(*b*) COEFFICIENT OF CUBIC EXPANSION.

The coefficient of cubic expansion permits the calculation of the volume and specific gravity of an oil at different temperatures. If these have been determined at some convenient temperature, a knowledge of this coefficient allows the calculation of the volume and specific gravity at some standard temperature such as 60° F. (15.56° C.). The significance of this procedure in dealing with bulk quantities of oils has already been pointed out under (*a*).

Each kind of marine fatty product probably has its individual coefficient of cubic expansion, which is known to vary sometimes even among different samples of one type of product. There is an appreciable difference between the coefficient of a liquid fat and that of the same fat in the solid state, and the coefficient of either varies slightly with the temperature. This slight variation with temperature is usually ignored by employing the *average coefficient of cubic expansion* for the range of temperatures likely to be encountered in practice, but it should be emphasized that the average coefficient for a liquid oil or a solid fat does not apply over the transition range of temperatures at which the oil is solidifying or the fat is melting, for reasons mentioned later.

The numerical value of the average coefficient of cubic expansion for a completely liquid fish oil between 59° and 120° F. (15° to 50° C.) lies in the vicinity of 0.00045 per degree Fahrenheit change in temperature. This may be approximately interpreted as stating that an oil expands (or contracts) to the extent of 0.00045 of its original volume for each degree Fahrenheit rise (or fall) within the given temperature range. The coefficient per degree Centigrade is 1.8 times as great as the coefficient per degree Fahrenheit.

Providing no change from liquid to solid state (or *vice versa*) takes place within a temperature range $t°$ to $T°$, for which the average coefficient, k, is known, the following relations are sufficiently accurate for most practical purposes and apply to increase or decrease in temperature if the algebraic rules for addition and subtraction are observed. If temperatures are expressed in the Centigrade scale, the appropriate k must be used.

$$\text{Volume at } T° = \text{volume at } t° \times [1 + k(T° - t°)]$$
$$\text{Spec. grav. at } T° = \text{spec. grav. at } t° \times [1 + k(t° - T°)]$$

To compare the weights of a fixed volume of material when at two different temperatures, the second of the above relations may be used by reading "weight" for "spec. grav."

Somewhat divergent and discordant numerical values for the coefficients of common marine animal oils are reported by different investigators. Representative values collected from various sources are presented in table **XX**.

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Oil	k per °F.	k per °C.
Whole fish oils		
Menhaden..................	0.00036 to 0.00039	0.00065 to 0.00070
Sardine....................	0.00044	0.00080
Herring....................	0.00044	0.00079
Pilchard...................	0.00042	0.00075
Liver oils		
Cod.......................	0.00038	0.00069
Basking shark..............	0.00036	0.00065
Blubber oils		
Whale.....................	0.00039 to 0.00042	0.00070 to 0.00075
Seal......................	0.00034 to 0.00036	0.00062 to 0.00065
Porpoise..................	0.00036 to 0.00039	0.00065 to 0.00070

The values shown for herring and pilchard oils were determined in these laboratories from typical commercial samples produced in British Columbia, and represent the coefficient over a range from 100° F. to the lowest temperature at which the oil remained clear. In the case of some values reported by other investigators it is not evident whether the oil was entirely free from stearine.

The presence of separated stearine in an oil has an immediate effect of apparently increasing the coefficient during either cooling or warming. This is partly attributable to the phenomenon mentioned under (a), namely that the stearine occupies less volume (i.e. has a higher specific gravity) than the oil at the same temperature. Since the fat is not a simple chemical compound but rather a complex mixture, there is no sharp freezing or melting point, and consequently the separation or melting of the stearine takes place gradually with an apparent effect of increasing the rate of volume change per degree change of temperature. Determinations made in these laboratories (Carter 1937, 1938) on pilchard and herring oils containing stearine between 32° and 68° F. (0° and 20° C.) showed that the apparent coefficient under such conditions is about 0.0006 per degree F. (0.0011 per degree C.). These results tend to confirm those of Bolton and Williams (1935) who point out the errors arising in commercial practice due to using faulty coefficients in estimating the weight of shipments of oil. No more exact figure can be quoted as the expansion and contraction in the presence of stearine is irregular and the coefficient varies with the amount of stearine present. The coefficient for *completely solid* stearine is not greatly different from that of the oil.

Figure 14 illustrates the volumes and specific gravities obtained experimentally as the temperature of a solidified sample of herring oil was raised very slowly from 33° to 100° F. and the then liquid oil was very slowly cooled over the same range. It will be seen that, on warming, the gradual melting of the stearine plus its expansion on heating gave rise to a rate of volume increase

(or specific gravity decrease) corresponding to a coefficient of expansion of about 0.0006 as indicated by the rough parallelism of the rising temperature curve to the line representing that coefficient in the upper key. The last trace of stearine melted at about 94° F. On cooling, the straight upper portion of the falling temperature curve indicates that the oil remained liquid to about 67° F. and exhibited a coefficient of contraction of about 0.00044; below that temperature there was a sudden contraction due to stearine formation after supercooling (see page 161), followed by a resumption of the coefficient 0.0006 as more stearine separated and cooled. The lower portions of the two curves do not coincide due to hysteresis effect.
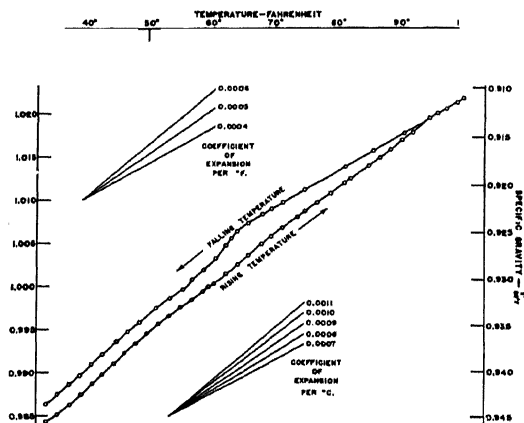
FIGURE 14. Effect of stearine on coefficient of cubic expansion, volume and specific gravity of sample of British Columbia herring oil undergoing very slow heating and cooling.

The use of a wrongly assumed coefficient of expansion gives rise to relatively small errors in computing specific gravities, volumes or weights of given volumes, as compared with the errors introduced by neglecting entirely the effect of temperature on these properties. The error introduced by using a coefficient 0.0005 instead of 0.0004 for a 20° F. temperature difference is about 0.2 per cent as compared with an error of about 1° per cent if the temperature effect were ignored.

Figure 15 shows the relationship between temperature and specific gravity of a certain sample of pilchard oil between 68° and 149° F. (20° and 65° C.). The relationship is seen to be linear over this temperature range and could safely be extended to 212° F. (100° C.). From this graph the specific gravity of other samples of completely liquid pilchard oil at various temperatures may be found, provided that the value at one temperature is known. This value would be plotted as at A in the graph and a line drawn through this point

parallel to the original curve, as indicated by the sample dotted line through A in the figure. The specific gravities of the new oil may then be read from the new line for any temperature between the limits shown. The data from which figure 15 was drawn showed that the sample of pilchard oil had a coefficient of cubic expansion equal to 0.000415 per °F. (0.00075 per °C.).
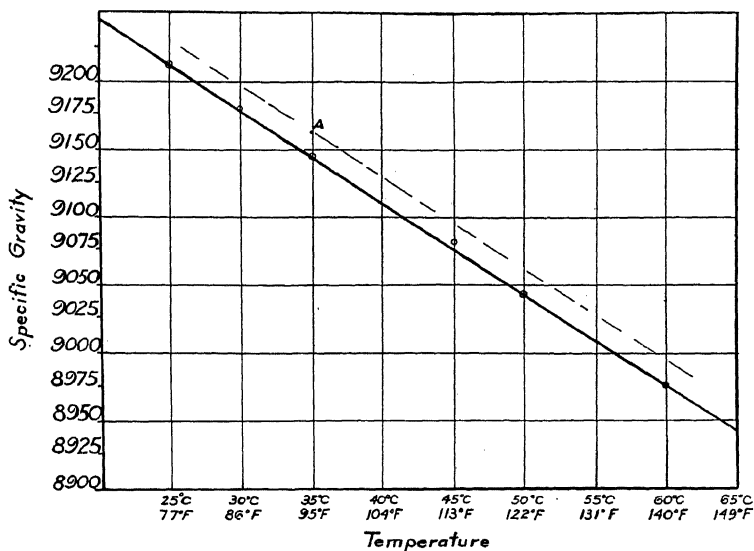
FIGURE 15. Specific gravity of pilchard oil at various temperatures.

(c) MELTING POINT.

The normal melting point of a substance is the temperature at which the substance changes from a solid to a liquid on being heated at atmospheric pressure. The majority of pure individual crystalline substances, when small amounts are very slowly heated, undergo a sudden transition from solid to liquid that allows the temperature at the melting point to be observed with great accuracy, thus serving as a valuable means of classifying or identifying the substance. All of the individual glycerides and practically all of the various non-saponifiable constituents of marine animal oils, if isolated and purified, are either crystalline at ordinary room temperature or may be brought into crystalline form at lower temperatures, and therefore have characteristic melting points. Unfortunately, the individuality of the melting point of the individual constituents can seldom be recognized or made use of when dealing with the natural oils and fats, due to the extreme complexity of the mixtures of these constituents in the natural products. Thus the term "melting point" as applied to such products loses part of its true significance and assumes a more general, technological interpretation.

The nature of the melting point of a substance may be affected by several

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circumstances. Under the three headings which follow, those factors that most concern the melting of natural fats and their individual chemical constituents will be treated briefly.

Admixture of other substances. The melting point of a solid is practically unaffected by the presence of particles of other materials which are insoluble in the original substance in its liquid state. If, however, two or more substances are partially or completely soluble in each other in the liquid state, each exerts a lowering effect on the melting point of the other and the melting point of the solidified mixture will lie between or below the melting points of the pure components.
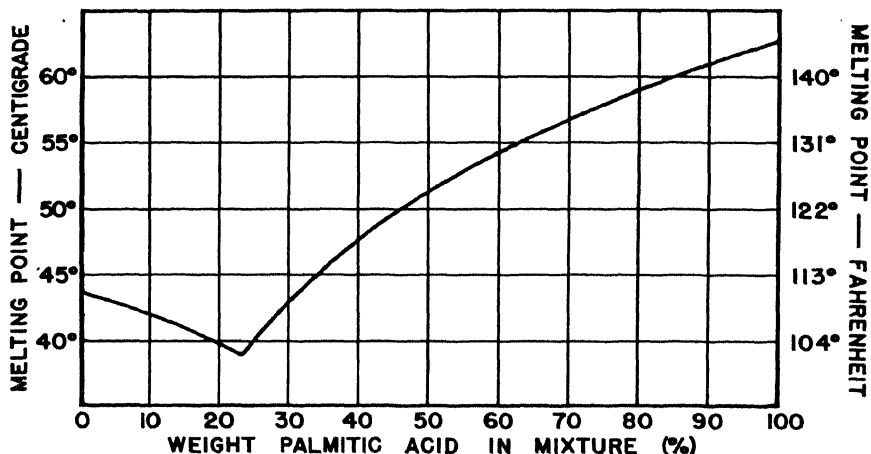
FIGURE 16. Melting points of mixtures of palmitic and elaidic acids, showing lowering of melting point and eutectic formation.

Figure 16, adapted from the data of Smith (1939), illustrates how the melting points of mixtures of two pure fatty acids solidified from a mixture of the liquid acids in various proportions vary. The corresponding phenomena for mixtures of three or more components are too complex to be described here. This diagram shows that mixtures containing 30 per cent or more of palmitic acid (melting point 63° C.) with elaidic acid (melting point 44.5° C.) have melting points lying *between* those of the pure acids, and that mixtures containing up to about 30 per cent of palmitic acid have a melting point *below* that of either component. The melting of such mixtures generally does not take place at a sharply defined temperature, but rather over a small, indefinite temperature range. This phenomenon of the *lowering of the melting point* is of significance not only for its gross effect, but also as a means of estimating the purity of a crystalline substance, for if the temperature and sharpness of the melting point can be increased by any operation, this is an indication that a second constituent

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(as an impurity) is being removed. Stearic acid present to the extent of 1 per cent as an impurity in oleic acid lowers the melting point of the latter by 0.13° C.

The lowest melting point on the curve shown in figure 16 corresponds to a mixture containing about 23.8 per cent palmitic acid. This particular mixture is known as a *eutectic*, which behaves in many ways as though it were a chemical compound of palmitic and elaidic acids, though such is not the case. Eutectic mixtures of some fatty compounds possess quite sharp melting points and as they sometimes resist simple efforts to separate the two components, they have on occasion been mistaken for new chemical entities. Not all mixtures of fatty compounds, however, form eutectics.

Careful inspection of the change in melting point as the ratio of two fatty acids in a mixture is altered has revealed that actual chemical compounds may be formed in some cases, though these are unstable and apparently have little significance in the technology of fats.

Pressure. At atmospheric pressure, a pure solid cannot be heated above its normal melting point. If the solid expands on melting, as do most fatty compounds, an increase (or a decrease) in pressure raises (or lowers) the melting point; for fatty acids above C_{12} the melting point is raised approximately 0.0225° C. (0.04° F.) for each increase of one atmosphere of pressure (14.7 lb. per sq. in.). The corresponding value for glycerides is similar. This effect of pressure can assume significant proportions in the hydrogenation of fatty materials under high pressure.

Stable and unstable modifications of a solid. Pure fatty triglycerides have been known for many years to display erratic melting points. Recent work by Carter and Malkin (1939) has shown that many triglycerides are capable of existing in four modifications in the solid state, one unstable vitreous form and three crystalline forms. In any one triglyceride each form has its own melting point, as exemplified by unsymmetrical palmitodilaurin, which displays the following four melting points depending on rate of heating and previous thermal history of the sample: Unstable vitreous form, m.p. 20° C.; unstable α-crystalline form, m.p. 33° C.; unstable β'-crystalline form, m.p. 43° C.; stable β-crystalline form, m.p. 46.5° C. Symmetrical triglycerides appear to exist in only three modifications. For example, tristearin after being slowly cooled melts at about 72° C.; if the liquid is quickly chilled, the unstable vitreous solid formed first melts at 54° C., then re-solidifies. A third form (unstable) melts at 65° C.

The process of melting requires the absorption of heat, called *latent heat of fusion.* When a pure crystalline substance in bulk is steadily heated, its temperature rises steadily until its melting point is reached. Its temperature then remains almost constant (practically so if stirred) while the heat of fusion is being absorbed. Finally, after all the solid has melted, its temperature again rises steadily. The same applies when a eutectic in bulk is heated; but in general, when a bulk solid mixture of two or more substances (e.g. a natural fat) is heated, the process of melting extends over a considerable temperature range and a gradual softening is followed by the appearance of a liquid containing

suspended crystals. The last trace of crystals of a high-melting constituent may persist until the melting point of that constituent is almost attained. A typical example is the melting of stearine.

Elsewhere in this Bulletin are recorded the comparative melting points of various types of pure fatty compounds (i.e. fatty acids, table I) and certain natural marine animal fats. Some estimate of the melting points of the stable form of the various triglyceride components of these fats may be obtained from the data and generalizations in table XXI.

TABLE XXI. Comparison of melting points of some fatty acids and their triglycerides.

Fatty acid	Lauric, C_{12} saturated	Myristic, C_{14} saturated	Palmitic, C_{16} saturated	Stearic, C_{18} saturated	Oleic, C_{18} mono-ethylenic	Linoleic, C_{18} di-ethylenic
Melting point of fatty acid (°C.)..........	43.5	53.8	62.9	69.6	16	−8
Melting point of fatty acid triglyceride(°C.)	46.4	57.0	65.5	71.5	5	−12

The saturated "simple" triglycerides (figure 1) thus melt about 3° C. higher than the fatty acid from which they are formed, and the longer the carbon atom chain of the saturated fatty acid, the higher the melting point. Increasing unsaturation in the fatty acid portion has a considerable lowering effect on the melting point.

For the types of triglycerides predominating in natural fats, namely those formed from two or three different fatty acids (the "mixed" triglycerides of figure 1), it may be stated in general that: (1) The melting point is usually lower than that of the "simple" triglyceride of the lowest-melting fatty acid combined in the "mixed" triglyceride. (2) The melting point may be lower than that of the lowest-melting fatty acid forming the triglyceride. (3) A "mixed" triglyceride having its fatty acid radicals symmetrically attached to the glycerol portion melts at a temperature slightly higher than that of its isomer in which the acid radicals are unsymmetrically arranged. (4) The greater the number of unsaturated linkages in the triglyceride, the lower the melting point.

(*d*) FREEZING POINT.

The normal freezing point of a substance is the highest temperature at which the substance changes from a liquid to a solid state on being cooled at atmospheric pressure. The effect of pressure has already been mentioned in II (*c*) of this Section.

The freezing point of a substance is frequently identical with its melting point, but not always, particularly in the case of fatty substances. This is due

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to the possibility that an unstable crystalline or vitreous modification having a freezing point different from that of the stable modification may first appear on cooling. Moreover, the first appearance of the solid on cooling may take place at a temperature considerably lower than the true freezing point; for, whereas a crystalline solid cannot be heated at atmospheric pressure above its melting point without melting, many liquids may be cooled below their freezing point without freezing. The latter phenomenon is known as *supercooling*. When a supercooled liquid in bulk finally commences to crystallize during cooling, the temperature rises and remains fairly constant during solidification, due to the liberation of the same quantity of heat (latent heat of fusion, page 159) that the same weight of substance absorbed during melting. The temperature of the solid then falls on further cooling. Water may be supercooled several degrees below its freezing point, and many fats, particularly natural complex fats, tend to supercool very readily (e.g. delayed separation of stearine). Glycerol, a constituent of all fats, affords a very striking example of the tendency towards supercooling, for although the pure substance melts at 18° C. (64.4° F.), it is rarely seen as a solid, even in the coldest weather.

The true freezing points of the pure fatty constituents of marine animal oils are sufficiently close to their melting points to allow the observations concerning lowering of melting point by admixture, and magnitude of melting point, as given in II (c) of this Section, to apply to the corresponding freezing point phenomena when precautions against supercooling are observed.

In the case of natural oils, however, the complexity of the freezing phenomena due to mixtures causes the true freezing point to be of little technical significance, and an empirical substitute known as the "titre point" [Part II (e) of this Section] is employed in oil and fat technology.

Stearine formation, cold tests and cold-clearing in connection with marine animal oils all depend on the freezing phenomena described above. Rate of cooling, supercooling, viscosity of the oil in which freezing is taking place, and concentration of nuclei of crystal growth are important factors affecting the apparent freezing point. Carter (1938) has shown in these laboratories that a clear sample of British Columbia herring oil could be rapidly cooled to 10° C. (50° F.) and held for 10 minutes at this temperature without stearine freezing out; on cooling the oil to 21° C. (69.8° F.), no stearine separated for over 30 minutes; yet on warming the solidified oil, the last crystals of stearine did not melt until the temperature rose to 35° C. (95° F.). As described in Section 8 I (b) other workers in these laboratories have shown that the amount of stearine separated when pilchard or herring oil is very slowly cooled to a given temperature depends on the rate of cooling, even when as slow as 2° and 4° C. (approximately 3° and 7° F.) per day. The extreme slowness at which all the stearine capable of freezing at a given temperature separates out is also emphasized. These effects have a profound significance in the technology of marine animal oils, and also have a bearing on the quantity measurement of such oils due to the volume changes that take place during stearine formation and melting [Section 5 II (a) and (b)].

(e) TITRE POINT

The titre or setting point is the highest temperature in degrees Centigrade reached whilst fatty acids solidify from the melted state. As the fatty acids are cooled, the temperature drops until solidification begins, after which, owing to the liberation of the latent heat of fusion, the temperature of the melt remains constant for a few moments and then slowly rises. The highest point reached is the titre point. Although the same procedure may be used for fats or oils, the rise in temperature is not so well defined as in the case of the fatty acids themselves and the titre point is therefore practically always determined on the latter material.

The titre or setting point is an important physical constant much used in industry for specifying quality of fats or fatty acids for use in soap, lubricants, cosmetics, etc. The titre point of a mixture of fatty acids is affected by the complexity of the mixture and the nature of the fatty acids. Work on mixtures of more or less pure fatty acids indicates the impossibility of determining composition from this characteristic. Jennings (1932) investigated the titres of binary mixtures of lauric, myristic, palmitic and oleic acids and found the titre-composition curve to vary in each case. Binary mixtures of lauric-myristic, lauric-palmitic, and lauric-oleic acids gave pronounced minima in the curves whilst oleic-palmitic and oleic-myristic gave definite maxima. With more complex mixtures such as occur in natural fats and oils, no attempt has yet been made to correlate composition with titre.

The titre point is profoundly affected by unsaturation and it is in this direction that it has been most used in industry. In any one kind of animal or vegetable fat or oil, the proportion of fatty acids of different carbon content remains constant within fairly narrow limits; the average unsaturation, however, may vary over a wider range. Titre data for a large number of samples of beef tallow, for instance, show that there is a fairly close relationship between this value and the average unsaturation as measured by the iodine value. The same is true for a large number of fats such as lard, mutton tallow, etc. In the case of fish oils the titre point is of some importance in specifying properties of the hydrogenated product. Unless the composition of the fatty acids according to carbon groups is quite similar for two or more fish oils, it becomes necessary to construct a titre-iodine value curve for each individual oil and even then, seasonal or other changes in the carbon composition may alter the type of curve of any one kind of oil. Swain (1939, unpub.) has investigated the relationship between the titre and iodine value of hydrogenated samples of salmon, herring and pilchard oils. The data are shown in figure 17. All three oils showed a peculiar phenomenon during the earlier stages of hydrogenation, in that the titre point actually *decreased* during the initial decrease in iodine value of 20 to 80 units. It is known of course that during this period of hydrogenation the more highly unsaturated fatty acids are selectively reduced to mono- or di-ethylenic acids with little if any formation of solid saturated acids. Just why this particular change in composition should reduce the titre point is not

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known at present and the matter is being investigated further. After the initial hydrogenation period the titre point increases with decrease in saturation. The rate of change is not quite linear and with each oil there is a tendency for the titre point to increase more slowly at the higher stages of saturation. In the case of pilchard and herring the highest titre obtainable is about 53° C., while in the case of salmon oil it may reach 56° C. The differences in the titres of the fully hydrogenated products are most likely due to the differences in the proportions of the fatty acids of various carbon contents. It is interesting to note, however, that samples of herring oil produced in more northerly waters (i.e. Alaska) give fully hydrogenated fatty acids with titres 56° C. and over. The herring oil used in the present work was produced in British Columbia and so
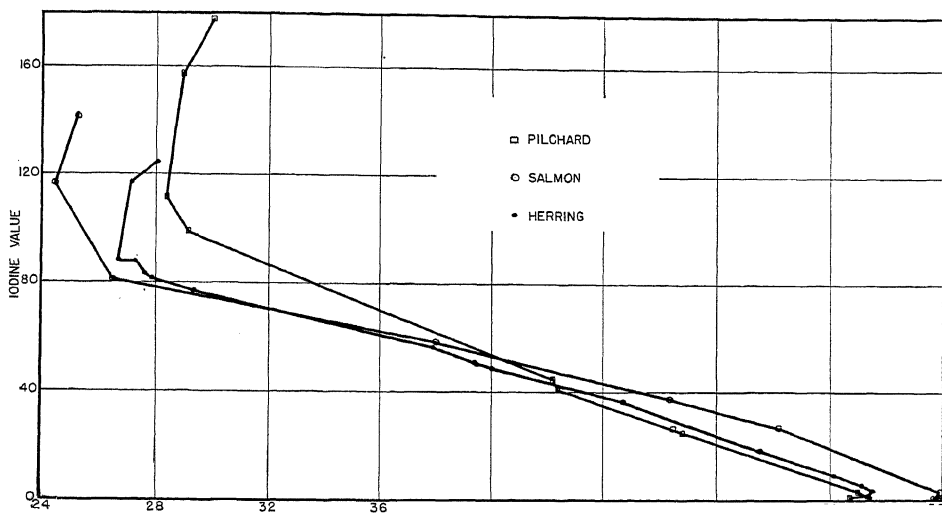
FIGURE 17. Relation between titre and iodine value in several hydrogenated fish oils.

far no herring oils from this province have yielded fully hydrogenated fatty acids with titres higher than 53° C. A comparison of the compositions of Alaska and British Columbia herring oils is now being made in an attempt to explain these differences in titres.

(f) BOILING POINT AND EFFECT OF REDUCED PRESSURE

Boiling of a liquid occurs when the application of heat has raised the vapour pressure of the liquid until it equals atmospheric pressure which, at sea-level, is equal to the pressure (14.7 lb. per sq. in.) of a column of mercury 760 mm. (29.9 in.) high. The temperature at which boiling occurs under 760 mm. pressure is called the normal boiling point. If the pressure is made greater by confining the vapours, the boiling point is raised. The boiling point is lowered if the

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pressure is decreased by increase in altitude above sea level, or by application of some degree of vacuum.

The normal boiling point of fats is usually so high (over 570° F. or 300° C.) that polymerization or decomposition takes place before it can be reached. Some fatty components and derivatives, such as fatty acids, esters, hydrocarbons and fatty alcohols, can be distilled at atmospheric pressure without decomposition, but, since the boiling point increases by 27° to 33° F. (15° to 18° C.) for each additional carbon atom in the carbon atom chain, the following compounds represent the upper limit of carbon chain length and the corresponding boiling point at which distillation under atmospheric pressure is practicable:

Saturated straight-chain fatty acids: C_{12} 563°F., 295°C.
Saturated straight-chain fatty acid methyl esters: C_{12} 487°F., 253°C.
Saturated straight-chain fatty alcohols: C_{12} 491°F., 255°C.
Saturated straight-chain fatty hydrocarbons: C_{16} 549°F., 287°C.

Corresponding unsaturated fatty compounds boil at similar or slightly higher temperatures, and are more prone to polymerization and decomposition.

To avoid the changes and decomposition attending the distillation of fatty compounds having twelve or more carbon atoms in the chain, which include the majority of fatty compounds derivable from marine sources, distillation under reduced pressure is employed. Such distillation may be desired for purposes of purification, identification, or separation of the components in mixtures.

TABLE XXII.   Effect of reduced pressure on boiling point of fatty compounds.

	Pressure (mm.)	Boiling point (°F.)	(°C.)
C_{18} acid (stearic).........	100	556	291
	15	450	232
	1	320	160
C_{18} acid methyl ester.....	15	419	215
	1	309	154
C_{16} alcohol (cetyl)........	760	651	344
	15	374	190
	1	268	131
C_{18} alcohol (stearyl)......	15	410	210
	1	302	150
C_{18} hydrocarbon (pristane).	760	565	296
	10	316	158
C_{30} hydrocarbon (squalene)	25	545	285
	15	520	271
	0.5	401	205

There is no simple way of calculating the boiling point at any given reduced pressure unless the boiling points at two or three other pressures are already available. Figure 18 illustrates the effect of reduced pressure on the boiling point of a saturated fatty acid ·(caprylic, $C_8H_{16}O_2$) which can be distilled at atmospheric pressure without decomposition. Other fatty compounds give rise to pressure—boiling point curves of similar shape, except that the curves fall on a different portion of the temperature scale. Table XXII gives an indication of the lowered boiling points of several types of fatty compounds which, due
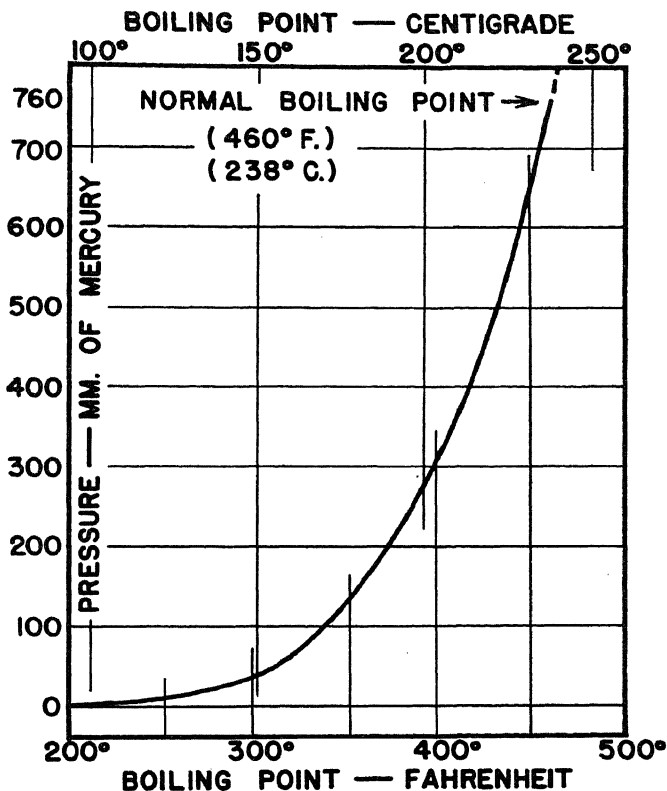
FIGURE 18. Effect of reduced pressures on boiling point of a fatty acid (caprylic, $C_8H_{16}O_2$).

to their greater molecular weight, tend to decompose before their normal boiling point is reached. Data for other fatty acids will be found in tables I and II.

Natural fats, being mixtures, have no definite boiling point under reduced pressure; on being distilled under extremely high vacuum the separation of certain impure saturated triglycerides such as trilaurin (at 500° to 525°F.), trimyristin (at 550° to 570°F.) and tripalmitin (at 590° to 610°F.) has been effected.

Another method of distilling below the normal boiling point is that of

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molecular evaporation under an extremely high vacuum. The substance does not actually boil, but evaporates rapidly across a narrow space between heated and cooled surfaces. By means of this method vitamins and fatty hydrocarbons are now being evaporated from fish and fish liver oils on a commercial scale. Vitamin A thus evaporates at 279° F. (137° C.) when the pressure has been lowered to 0.00001 mm. of mercury.

A third method of distilling below the normal boiling point depends on the principle that when a mixture of two completely immiscible liquids is boiled at atmospheric pressure, each boils below its normal boiling point. Thus when myristic acid (boiling normally at about 605° F. with some decomposition) is heated with excess water or steam at atmospheric pressure, the steam at slightly below 212° F. contains about 0.2 per cent by weight of acid, which is readily separated from the condensate. By superheating the steam, the proportion of acid is raised to 7.17 per cent, and, by reducing the pressure to 38 mm., the steam at about 90° F. contains 65.7 per cent of acid. Steam distillation is used commercially to a great extent in the separation of fatty acids from hydrolyzed oils.

(g) REFRACTIVE INDEX

When a beam of light passes from air into a denser medium such as water or oil, it is refracted towards the normal, i.e. a line at right angles to the interface. The ratio of the sines of the angles of incidence and refraction is constant at the boundary of any two media. This ratio is called the refractive index and is usually measured with air as the lighter medium. The refractive index is an important physical property that, in the case of oils, is used as an analytical tool.

The refractive index of a substance decreases with increase in temperature but this decrease is due to the decreased density. If the density of the substance is taken into consideration, then the refractive index is practically unaffected by temperature. In the case of oils and fats, the refractive index depends upon the molecular weight and degree of unsaturation of the component fatty acids, increasing with increase in molecular weight and also with the number of double bonds in the fatty acids. Fatty acids containing hydroxyl groups have a higher refractive index than those containing a similar number of double bonds. Furthermore, it is well known that double bonds in the conjugated position produce a large increase in refractive index. Finally, the refractive index of a neutral fat or oil is higher than that of the total free fatty acids.

There is a close relationship between the refractive index of an oil and the unsaturation as measured by the iodine value. If a series of oils is prepared from the same sort of material by identical methods, then the unsaturation in terms of iodine values can be calculated quite accurately from the refractive index. Recently, Harrison *et al.* (1939) investigated the refractive indices and iodine values of 169 samples of oil from five species of salmon from widely varying localities. They found that there was a positive correlation of 0.9747

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between these two characteristics and suggested that the iodine value could be calculated by the equation

$$\text{Iodine value} = 6{,}929 \times n_D^{25} - 10{,}079.2$$

In the process of hydrogenation the double bonds become saturated and the refractive index decreases. The use of this latter value has thus become of importance for rapidly estimating the degree of saturation during the hydrogenation process. Brocklesby and Charnley (1933) found that during the hydrogenation of pilchard oil the relationship between refractive index and iodine value could be expressed by the equation:

$$n_D^{60} = 1.4474 + 9.6158 \times 10^{-5} I \times 10^{-8} I^2$$
$$\text{(where } I = \text{iodine value)}$$

As pointed out in other sections of this Bulletin, oxidation and polymerization of unsaturated oils both increase the refractive index. Pickering and Cowlishaw (1922) claim that by taking into consideration the acid and saponification values the refractive index can be calculated from the equation:

$$N_D = 1.4643 - 0.000066 \text{ (sap. val.)} - 0.0096 \times \text{acid val./sap. val.}$$
$$+ 0.000117 \text{ (I val.)}$$

These authors state that if the refractive index of any sample, after correction for acidity and saponification value, lies above the curve for the iodine value found, it is certain that the sample is not fresh. In other words, the plot of the above equation furnishes a means of detecting incipient oxidation. The increase in refractive index during the polymerization of fish oils has been discussed by Brocklesby and Denstedt (1934).

Refractive index measurements have also been used to determine the oil content of seeds and other oil-bearing materials. It is based on the change in refractive index taking place in a solvent when a known weight of the dried material is extracted with a definite quantity of the solvent. Geddes and Lehberg (1936), working with dried flaxseed and halowax, found that the correlation between the halowax-extract scale reading and ether extractions was 0.95 and that the standard error of prediction of the oil content by the refractometric method was 0.59 per cent. It might be emphasized that any solvent chosen for the refractometric determination of oil content of tissues should be one that is not associated. Brocklesby and Carter (unpub.) have investigated the density and refractive index relationships of solutions of raw and polymerized oils in cyclohexane and dioxane. Both raw and polymerized oils in cyclohexane gave solutions the densities of which were a linear function of the volume concentration. The refractive indices deviated slightly from strict linearity which was caused by slight volume changes that were probably undetected by the density determinations. The specific refractivities, however, followed a strictly linear relationship to the weight concentration. In dioxane both the raw and polymerized oils showed densities that were not a linear function of the volume concentration, both curves becoming concave to the axis with a maximum deviation at about 50 per cent volume concentration. Refractive indices showed the same type of curve, but the deviation from linearity was greater in the case of the polymerized oil than in that of the raw oil. The specific refractivities were again an exact linear funtion of the weight concentration. It was apparent that in the dioxane solutions there was an increase in volume following the mixing of the two components. This increase attained a maximum of 0.57 per cent at 50 per cent volume concentration.

(h) Viscosity

When a liquid moves through a tube all parts of the liquid do not move at the same velocity; the layers near the wall of the tube move more slowly than those nearer the centre. There is thus a shearing action of these layers past one another and the force which opposes the relative displacement of the layers of the liquid is the internal resistance or viscosity of the liquid. In the case of lubricating oils this viscosity is a very important physical property and it is also used to a certain extent to measure the changes taking place during the blowing or heat-treatment of drying oils. It is not used very much in connection with oils intended for other industrial purposes.

The viscosity of oils is affected by the nature of the component fatty acids, particularly the ratio of the saturated solid fatty acids to unsaturated liquid acids. Oils containing fatty acids with a hydroxyl group are usually more viscous than those lacking such acids. The manner in which the fatty acids are linked to the glycerol molecule seems to be of some importance as far as viscosities are concerned. Oils with similar fatty acid compositions may not have similar viscosities due to differences in the actual glyceride structures. As a consequence, iodine values, that are a measure of the average unsaturation, do not always show a linear relationship to viscosity. Materials that may have a profound effect on the viscosity of oils are the non-fatty components such as lecithin. Oils containing large amounts of phospholipides are usually more viscous than those with smaller amounts.

The viscosity of oils decreases rapidly with increase in temperature, but the relationship is not a linear one; with increase of temperature the rate of decrease in viscosity increases. With increase of temperature the differences between the viscosities of different oils tend to decrease. Polymerization and oxidation both increase the viscosity of oils.

TABLE XXIII. Viscosities of s   fish oils in centipoises

Kind of oil	Observer	
	Brocklesby (25° C.)	White (30° C.)
Commercial salmon..........................	45.2	
Commercial herring.........................	37.7	
Commercial whale..........................	43.3	34.8
Commercial sperm whale...................	23.6	33.3
Laboratory dogfish liver....................	48.4	39.9
Commercial pilchard		
Raw.................................	32.8	
Light pressed.........................	29.8	
Medium pressed.......................	29.6	
Heavy pressed........................	28.2	
Commercial menhaden (light)...............		29.6
Commercial menhaden (dark)...............		60.2
Cod liver..................................		38.8

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Some actual data on the viscosities of fish oils are given in table XXIII. Most of these were determined by the writer using a calibrated Stormer viscometer; the remainder are from a paper by White (1912) who used a capillary tube type of instrument. The data bring out one or two points of interest. Removal of stearine has a slight but measurable effect in lowering the viscosity, a greater difference being found between the raw and the light pressed pilchard oil than between the latter and the more heavily pressed oils. Salmon oil, although not being greatly more saturated than pilchard oil, has a much higher viscosity, probably on account of the higher content of phospholipides. The great difference between the two samples of menhaden oil is probably due to the difference in methods of extraction, the dark sample with the high viscosity being extracted by heating at 130° C. (266° F.) "whereby there was considerable
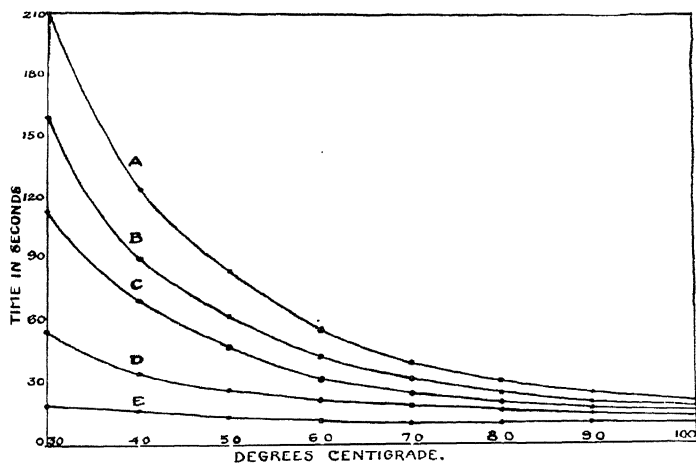
FIGURE 19. Temperature viscosity curves for pilchard oil polymerized for various times at 250°., as determined with Stormer viscometer. (Brocklesby and Sunderland, unpub.). A = 16 hours, mol. wt. 1660; B = 12 hours, mol. wt. 1500; C = 6 hours, mol. wt. 1217; D = 2 hours, mol. wt. 1200; E = raw oil, mol. wt. 900.

decomposition and the oil became quite gummy." Sperm whale oil is noted for its relatively low viscosity, a circumstance most likely related to the peculiar composition of this oil.

In figure 19 the effect of polymerization and temperature on the viscosity of a fish oil is shown. Polymerization markedly increases the viscosity and increase in temperature decreases it. The most important point to be noted, however, is that the temperature effect increases rapidly with increase in polymerization. The polymerized oil behaves as a colloid, the two dimensional linear polymers losing their gel characteristics as the temperature increases.

(*i*) SOLUBILITY

The solubility of an oil or fat in a solvent depends upon a number of factors, the chief of which are (1) the nature of the solvent, (2) the number of carbon

atoms in, and (3) the unsaturation of, the component fatty acids, and (4) the temperature.

Practically all marine animal oils are soluble in aliphatic or aromatic hydrocarbons such as petroleum spirits and ligroin or benzene and toluene. They are also soluble in the chlorinated hydrocarbons such as chloroform, carbon tetrachloride, ethylene dichloride, monochlorbenzene, etc. The ethers are also suitable solvents for marine animal oils, as also are the diethers such as dioxane. Alcohols and ketones are poor oil-solvents. The solubility improves, however, with increase in molecular weight of the solvent. Methyl and ethyl alcohol and dimethyl ketone in the cold do not readily dissolve oils but the higher members such as tertiary butyl and amyl alcohols and some of the higher ketones such as dipropyl ketone are very good solvents. Both the ketones and the alcohols have a high temperature coefficient. Organic acids are, as a rule, poor solvents for oils. Acetic acid has been used for analytical purposes particularly in attempts to differentiate various types of oils by their varying solubility in this liquid. Esters of low molecular weight acids and alcohols are poor solvents for oils but as the molecular weight of either the acid or alcohol part of the ester increases, the solvent power improves. The solubility of oils in ethyl acetate is rather low but in propyl and butyl acetate most oils are completely miscible.

Fatty acids are, in general, more soluble in a given solvent than the triglyceride and in most solvents the triglyceride is more soluble than the diglyceride. The solubility of fats or oils in a solvent also decreases with the increase in molecular weight of the component fatty acids; coconut oil is more soluble in petroleum spirits than is beef tallow; porpoise jaw oil is more soluble in alcohol than is cod liver oil. As the unsaturation of the component fatty acids in an oil increases, so does the solubility in any given solvent. If a fat containing mixed glycerides is shaken with a solvent such as alcohol or acetone in the cold the clear dilute solution will contain more of the unsaturated glycerides than the insoluble residue.

In all solvents the solubility of fats and oils increases with rise in temperature. As noted above, this is particularly noticeable in the case of the alcohols and ketones. Solid fats are much more soluble if heated in a solvent to a temperature above their melting point. Usually those solvents that are soluble in water are indifferent solvents for oils but a notable exception is that of the diether, dioxane, which not only will dissolve most oils but will also dissolve those that have undergone oxidation or polymerization.

It must be emphasized that the relative solubilities of various oils in a given solvent are very much influenced by the presence of impurities, either in the solvent or in the oil. This is particularly true of those oils containing varying amounts of such materials as lecithin. On the other hand, a high free fatty acid content in an oil will also give a fictitious value for solubility. The free fatty acids dissolve more readily than the neutral oil and the solution of the fatty acid in the solvent in turn acts as a better solvent for the remaining neutral

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oil. Statements regarding solubilities of oils in various solvents should always include a definite description of the purity of both the oil and the solvent.

(j) SURFACE TENSION ·

In the interior of any liquid the molecules are subjected to a molecular attraction that is exerted equally in all directions. The molecules at the surface, however, due to the lack of molecules above them, are subjected to a force directed towards the main body of the liquid, resulting in the so-called "skin effect" or surface tension. With respect to oils, this effect has not been studied extensively, the greater emphasis being placed on interfacial surface tensions between oils and other liquids and their bearing on the properties of emulsions. The importance of surface tension effects is well known in the lubricating industry and they are to some extent being studied in connection with other oil-using industries such as paint, leather and insecticide manufacture.

Surface tensions are measured in dynes per unit length of surface of liquid in a direction parallel to the surface. Due to the orientation of the glyceride molecules so that the hydrocarbon part of the molecule rests on the surface, the surface tension of practically all naturally occurring oils is of the same order of magnitude. Work in these laboratories shows that at 25° C. halibut head, herring, sperm whale and dogfish liver oils have surface tensions of 36.8, 37.1, 35.2 and 36.4 dynes per cm. respectively.

Temperature decreases the surface tensions of all liquids, this decrease being linear over the greater part of the temperature range. Canals and Ranaivo (1933) showed that the surface tension of cod liver oil varies linearly with the temperature according to the equation F (surface tension) $= 40.4 - 0.12T$ where $T =$ temperature in degrees Centigrade. Canals and Flous (1935) found that the surface tension of oils decreases with increase of free fatty acids. This decrease was very slight, however, a pure triglyceride showing a surface tension of 36.08 and the free fatty acids 35.44 dynes per cm.

In connection with the drying of linseed oil it has been stated that lead driers reduce and cobalt driers increase the surface tension of the oil. Measurements of areas and surface tensions on the so-called surface tension balance of mono-molecular films have been applied successfully to the elucidation of problems relating to the shape of large molecules, i.e., fatty acids and esters. A discussion of this phase of the subject is outside the scope of this Bulletin.

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SECTION 6. RANCIDITY IN MARINE ANIMAL OILS

I. NATURE OF RANCIDITY

(a) OCCURRENCE

It is common knowledge that practically all animal and vegetable fats and oils may undergo certain deteriorations which result in disagreeable odours and tastes. These changes are usually described by the term "rancidity", and are commonly met with in such fatty materials as lards, bacons, butters and other domestic commodities. Fisheries products are not exempt from the effects of rancidity. For instance, considerable losses are experienced through changes in the oil of fatty fish such as salmon and herring during cold storage: loss of palatability and vitamin potency of medicinal oils, and changes in the oil of fish meals during ordinary storage. These are but a few instances where rancidity spells loss to the fishing industry.

Rancidity, as far as the actual deterioration of the fat is concerned, really means the development of certain "off" tastes and odours, and does not necessarily infer that the product has become actually unfit for human consumption. In the past, and to a large extent even now, organoleptic, in preference to chemical tests, have been relied on to detect rancidity. Although the senses of taste and smell are notoriously unreliable, it has not been possible up to the present to find any one chemical test that will adequately detect the onset of rancidity in all types of fats and oils. Not all fats give the same type of odour or smell when they become rancid. For instance, when olive oil becomes rancid it develops a tallowy taste and odour, but under similar conditions, such oils as linseed and pilchard (more highly unsaturated) give a sharp, acrid odour. On the other hand, rancid milk and milk products are sometimes described as fishy. It is obvious that these several odours and tastes may not be due to the same products of decomposition.

The chief cause of rancidity is oxidation which may occur when the fatty material is exposed to the air, or when certain micro-organisms or enzymes are present. Other less important causes are the development of free fatty acids, the decomposition of nitrogenous material by bacteria, and the absorption of foreign odours.

(b) ATMOSPHERIC OXIDATION

Although atmospheric oxidation is the most serious cause of rancidity, actual continuous exposure to the air is not always necessary for this reaction to take place. Oils produced under usual conditions may have sufficient oxygen dissolved in them to bring about oxidation. Storing *in vacuo* or under an inert gas

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does not ensure against such an oxidation. Holm, Greenbank and Deysher (1927) have shown that a steamed oil, i.e. free of dissolved oxygen, stored *in vacuo* is much more stable than an untreated oil stored under the same conditions.

Since oxygen is the active agent in bringing about the more common types of rancidity, it is of importance to study both the rate of its absorption and the sequence in which the various oxidative products are formed. If the amount of oxygen absorbed by an oil is plotted against time, an S-shaped curve is obtained, which is characteristic of an "autocatalyzed" reaction (see figure 12, page 123). During the first period of exposure to air or oxygen, there is a slight but almost imperceptible absorption of oxygen. This is followed by a period during which apparently no oxygen is absorbed; in fact, under certain conditions the oil may actually appear to give up a portion of its oxygen, or other volatile constituents. Usually, however, the period during which no absorption of oxygen occurs is represented by a straight line parallel to the time axis, since under most experimental conditions any slight loss of volatile constituents from the oil is not detected. This quiescent period is followed by a rapid absorption of oxygen, the rate and extent of which depend upon the nature of the oil and the conditions of exposure. A comparison of the times taken for this rapid absorption to be reached for various oils under similar experimental conditions gives some indication of the relative susceptibilities of these oils to becoming rancid.

The mechanism of the oxidation of fats by atmospheric oxygen is explained in Section 5 I(*c*), but it might be well to recapitulate the essential points at this time. Briefly, oxygen dissolves in the oil to form a loose compound termed a "moloxide". This moloxide re-arranges itself to become a true peroxide. When the latter is formed, it decomposes in such a way that among the decomposition products is molecular oxygen which, being very reactive, immediately attacks the remaining double bonds. Formerly it was held that the induction period represented the time required for the formation of these peroxides. Later, however, it was shown that certain natural antioxidants were present in fats and oils and these substances inhibited the formation of the peroxides. Still more recent, however, is the interesting theory of Coe (1938), who suggests that rancidity is due to the photochemical activity of light. Chlorophyll in vegetable fats, and haemoglobin and other pigments in animal fats, are known to act as photosensitive substances, and Coe believes that under the action of light and oxygen these pigments cause the formation of an unstable form of hydrogen peroxide, which decomposes to form peroxides in the fat. According to this author, organic peroxides and the stable form of hydrogen peroxide do not enter into the reaction during the development of rancidity, and neither can they be used as a measure of the degree of rancidification. This theory supposes that the initiation of rancidity in oils is dependent on the action of light and the photosensitive compounds in producing nascent hydrogen peroxide. When the latter substance is formed, subsequent oxidation takes place independently of light. It is well known that practically all oils of both vegetable and animal origin become rancid more quickly in the light than in the dark, but the fact that they do become rancid in

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the absence of light, losing their induction period entirely, throws some doubt on the general applicability of this theory. It possibly explains the greater rate of rancidification in the presence of light, but the theory of natural antioxidants seems to be more in harmony with the facts of the general development of rancidity.

As indicated in Section 5, the products formed after the appearance of peroxides are very numerous and complex. They appear to vary with different oils and the conditions under which these oils become rancid. This circumstance possibly explains the lack of uniformity in the results obtained by various workers using different methods, each one of which measures a different oxidation product.

Methods for the determination of the degree of, or the susceptibility to, rancidity are very numerous. Obviously, as mentioned above, the measurement of the inductive period of an oil under fixed conditions appears to be one of the simplest of these methods, but due to certain interfering factors it is not widely used. Possibly the greatest objection to this method is the contention by many workers that the rate of oxygen up-take by an oil bears no constant relationship to flavour or odour. However, it serves for determining the relative stability to rancidity of the same oil treated in various ways.

A method used frequently in estimating the degree of rancidification of an oil is the determination of peroxide oxygen. Based on the formation of peroxides in the oil, this test gives a time curve similar to that obtained by the oxygen absorption method, and for that reason the beginning of rapid peroxide formation may be said to be analogous to the end of the induction period in the absorption of oxygen by an oil. While this test gives a positive reaction for all oils and fats, irrespective of composition, it of course has the disadvantage of all chemical tests, in that the amount of peroxides does not always agree with the results of organoleptic tests. This discrepancy is quite evident in figure 20, which shows the higher peroxide values obtained with greater unsaturation of an oil.

From this figure, also, it may be seen that the same is true of the Kreis value. The Kreis value has an added disadvantage, in that it fails to give a positive test for oleates, since oleic acid cannot give rise to epihydrinaldehyde, which is the decomposition product of unsaturated esters responsible for the characteristic red colour of the Kreis reaction, and presumably present only in a rancid fat. Despite the fact that the Kreis value has long been used as an official test for detecting rancidity, it would appear to be very unreliable. In these laboratories, several difficulties were encountered with its use, the chief being that after a certain—not very advanced—stage of oxidation had been reached, there was no increase in colour intensity.

Greenbank and Holm (1930) made use of the reduction of methylene blue by the oxidation of the unsaturated constituents of an oil in the presence of light. It is suggested that the dye acts as an acceptor of hydrogen from the oxidation of the oils. A modified form of this test has been used with success in these laboratories.

The foregoing tests have been considered in some detail, since they will be

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referred to again in connection with our own work on the rancidification of fish oils. Others which may be mentioned are Schiff's test for the presence of aldehydes, which are usually present as products of oxidation, Schibsted's test which is a more delicate form of Schiff's, and Issoglio's method of determining the amount of readily oxidizable steam-volatile substances present in a sample of fat. A newer method which is rapidly attaining prominence is the "Swift" test, which is a combination of the oxygen absorption and peroxide methods.
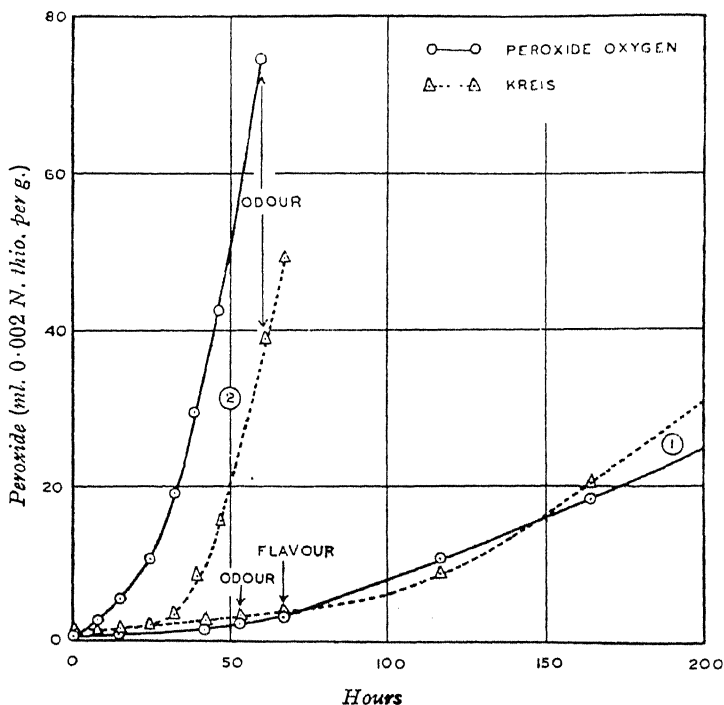
FIGURE 20. Influence of composition of the fat on values of the chemical tests on the appearance of rancidity. (1) Methyl oleate, (2) methyl oleate with linoleate (1:2). Exposed to lamp light at 26°C. (Barnicoat 1931).

The unreliability of the chemical tests for rancidity may be traced not only to fat composition but to the effect of various accelerators of oxidation. Such factors as light, temperature, peroxide content, acidity, traces of moisture, metals and metallic oxides all play an important role in the promotion of the rancidification of oils and fats.

For some years, light was considered to be essential, just as oxygen is, for the production of oxidative rancidity. It has now been established, however, that such is not the case, but rather that light is a very active accelerator of this reaction. Oxygen-free oils stored *in vacuo* in the presence of light remain per-

fectly stable, whereas untreated oils in the presence of light turn rancid very quickly. Even weak artificial light has quite a perceptible effect, although the most potent effect is obtained by ultraviolet light (wave lengths 2900-4000 Å), whilst the least effective is light of wave lengths 4700-5000 Å. Consequently, direct sunlight has tremendous accelerating properties on the rancidification of edible fats. Light is credited with having an autocatalytic action on oxidative rancidity, in that on increasing the time of exposure there results, on removal of light, an increase in the subsequent rate of oxidation; but this would appear to be due to the increased amount of active oxygen thus formed in the oil. It can readily be seen that light does play an extremely important part in rancidity, and it will be referred to again in the section on stabilization.

As is generally true of chemical reactions, the rate of oxidation of oils increases with rise in temperature. Storage at temperatures of 10°C. and lower, results in the increased stability of most oils and fats, although in the case of highly unsaturated fish oils, oxidation still takes place appreciably at this temperature—so that Tressler (1932) has recommended temperatures of −29°C. or lower as being necessary for adequate protection. Since for every rise of 10°C. the rate of oxidative rancidity is increased two or three times, the importance of low temperatures in oil stabilization is quite evident. This temperature coefficient varies, of course, with the temperature, increasing for higher temperatures and decreasing for lower temperatures, as well as being affected by the composition of the fat, the coefficient increasing as the unsaturation becomes greater.

We have already shown that the rate of oxidative rancidity is influenced by the amount of active oxygen present in the oil. In a partly oxidized oil, this takes the form of active peroxides, which may be molecules of peroxide recently formed so that they still retain the energy of formation, peracids, or loosely bound labile-peroxides. This peroxide content plays an important autocatalytic role in the development of further rancidity. These labile substances may be said to break down the natural inhibitors present and thus pave the way for further oxidation. Oils of high initial peroxide content will oxidize much more readily than fresh oils, and at an ever increasing rate, as the peroxide content increases.

The presence of free fatty acids in an oil has been claimed by some workers to have an accelerating influence on oxidative rancidity. Holm, Greenbank and Deysher (1927) report that small additions of acids to oils resulted in increased susceptibility to oxidation. On the other hand, Lea (1938) has recently found no such effect and questions whether free fatty acids do have any accelerating influence. He claims that the fact that mixtures of fatty acids oxidize more readily than their parent oil may be due to the removal of natural antioxidants in their preparation. It has also been shown that under certain conditions, oils may become rancid at a very low acid value. It is an open question, therefore, whether traces of free fatty acids do actually accelerate oxidative rancidity. However, in oils that have developed a high free fatty acid content in the presence of traces of moisture, it is usually found that oxidative rancidity has also taken place.

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Metals and metallic salts are a serious menace to oil producers, as they are powerful accelerators of oxidation. Commercial losses are experienced continually from their effect, as in soap rancidity and discoloration derived from the steel or brass dies of stamping machines, or in rancidity from storing in iron containers which have rusted or in tinned copper ones with the tin worn off. Brocklesby and Bailey (1935) have shown the detrimental influence of such containers on the production and storage of high-grade poultry oils, i.e. pilchard and herring oil. Iron and copper are the worst offenders in this way and their effect on the oxygen absorption of pilchard oil is shown graphically in figure 21. It has been stated that 0.8 parts per million of copper are quite sufficient definitely to accelerate oxidative rancidity. Apparently metals speed up the decomposition of
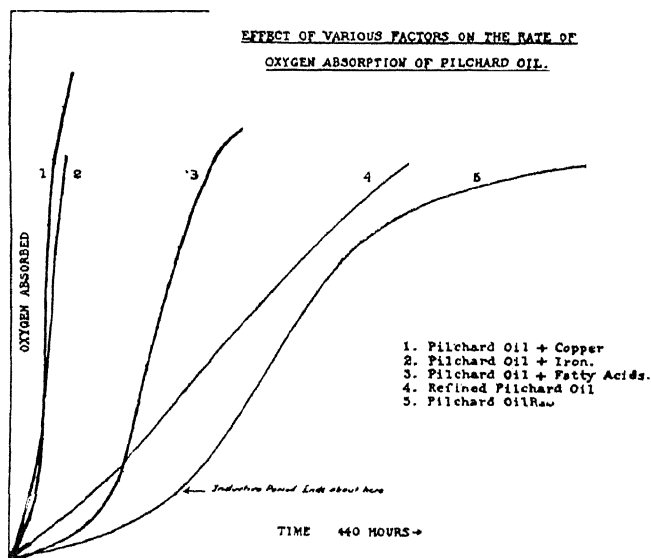
FIGURE 21.

natural antioxidants in the oil, and as well increase the rate of oxidation of the fat peroxides, all of which means a strongly accelerated rate of oxygen absorption and subsequent production of oxidative rancidity. Indeed, metallic salts in sufficient quantities appear to cause such a rapid oxidation that peroxides are completely eliminated from the reaction, the oxides being formed directly, as is seen in the action of driers on pilchard oil used for paints (Denstedt and Brocklesby 1936). These authors found that metals having a pro-oxidative action on pilchard oil may be listed in the following order of activity: cobalt, manganese, copper, iron, cerium, magnesium, aluminium, zinc, lead, and lead oxide; while those having little if any effect are nickel, tin and the cobalt-steels. Fabricated metals exerting barely any oxidative effect on oils are those which are highly resistant to cor-

rosion, as the nickel-chromium steels of the "staybrite" type. Copper should never be used for plant machinery which comes into contact with the oil, unless heavily coated with tin.

(c) Oxidative Rancidity of Fish Oils

Reference has already been made to the effect of fatty acid composition on the development of oxidative rancidity. This factor is of particular importance in the study of rancidity in fish oils because of the general complexity of their component fatty acids, many of which are highly unsaturated. These unsaturated acids oxidize very readily, and it has been claimed that the incipient oxidation products are responsible for the characteristic odour of fish oils. Even in fish oils that are relatively fresh, these odours are quite perceptible, and tend to mask those odours, which in less unsaturated oils would be ascribed to the development of organoleptic rancidity, and which may be said to be due, in most cases, to the products developed during the early oxidative stages of oleic acid. The more highly unsaturated acids must reach a more advanced stage of oxidation before a disagreeable odour and taste are produced. Consequently, comparisons of the development of organoleptic rancidity between fish oils and less unsaturated oils or fats are very difficult to make.

TABLE XXIV. Comparison of stabilities of various oils by different methods

Oil	Oxygen uptake[2] (hr.)	Peroxide value[3] (hr.)	Kreis test[4] (hr.)	Methylene blue[5] at 73°C. (min.)
Olive (84)[1]........	26	160	75	
Dogfish liver (114).	22	140	90	
Cod liver (164)....	5	50	50	10
Halibut liver (132).	2	12	..	2
Herring (137).....	3	45	50	11
Pilchard (179).....	2.5	36	51	6.5

[1]Numbers given in brackets denote unsaturation as given by iodine values.
[2]Measured by length of induction period.
[3]Measured by length of period of slow peroxide formation.
[4]Measured by length of period of slow red colour formation.
[5]Measured by time required for blue colour to be reduced to 4.0 Lovibond blue units.

From table XXIV by comparing the data on oxygen absorption, Kreis and peroxide values, some interesting conclusions may be drawn, not only of the effect of unsaturation, but also of the nature of the constituent fatty acids, and on the susceptibility of an oil towards oxidation. Fatty acids, in general, tend to become more reactive towards oxygen as the number of double bonds in the molecule increases. This is well shown by contrasting the stabilities of pilchard and olive oils, where there is a marked difference in degree of unsaturation.

The somewhat unproportional results obtained for cod liver, halibut liver

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and herring oils can be largely accounted for by the constitution of the component fatty acids. It is a matter of common observation that slight differences in structure will cause great variations in properties; Kuhn and Meyer (1929) have shown that elaidic acid (an isomer of oleic acid) is less readily oxidized than is oleic acid itself; while the introduction of an OH group, as in the oleic acid chain to form ricinoleic acid, results in a tremendous decrease in susceptibility towards atmospheric oxidation (Holm, Greenbank and Deysher 1927).

In the light of the above considerations, discrepancies such as those for cod liver oil and herring oil can be explained. While the gross unsaturation of cod liver oil is noticeably greater than that of herring oil, the constitution of its unsaturated fatty acids is probably different. The same reasoning may be said to apply to halibut liver oil, although in the case of the sample here reported it was produced by an alkali digestion process, the effect of which will be mentioned later. It will be realized, of course, that the age of the oils used, as well as the extent to which they have been subjected to the various accelerators of atmospheric oxidation, will all play important parts in determining their relative susceptibilities to oxidation. All oils used in these investigations were as fresh as could be procured, but naturally, conditions of production vary, which may in some cases account for differences in stability.

The reason for the disagreement between the three aforementioned tests and the methylene blue test is not clear at present, but would seem to involve the preferential absorption of the activating rays by the various pigments present in the oils.

TABLE XXV. Variations in methylene blue test for olive and pilchard oils

Olive oil			Pilchard oil		
Condition of oil	Exposure to light* (min.)	Reduction period at 67°C. (min.)	Condition of oil	Exposure to light* (min.)	Reduction period at 67°C. (min.)
Raw........		22	Raw........		12
"	30	17	"	30	7
"	60	12	"	60	5
Decolorized..		10	Decolorized..		3.5
" ..	30	6	" ..	30	2.5
" ..	60	4	" ..	60	1.5

*Before methylene blue was added.

Table XXV helps to give some idea as to the effect of pigments on susceptibility to oxidation as measured by the methylene blue reduction test. Removal of pigments by alkali refining and treating with carbon resulted in greatly decreased stability for both olive and pilchard oils. On the other hand, light plays an equally important part in its direct effect, for it is seen that on exposing the oil samples to the same light source as used for the test, before adding the methy-

lene blue, the subsequent action is considerably accelerated. So not only do pigments play a part here, but also there is the direct accelerating action on oxidation due to light. While the methylene blue test cannot be used to compare oxidative susceptibilities of various oils, it does prove a useful test for different samples of the same oil, as it emphasizes factors such as those mentioned. Further use will probably increase its reliability and importance.
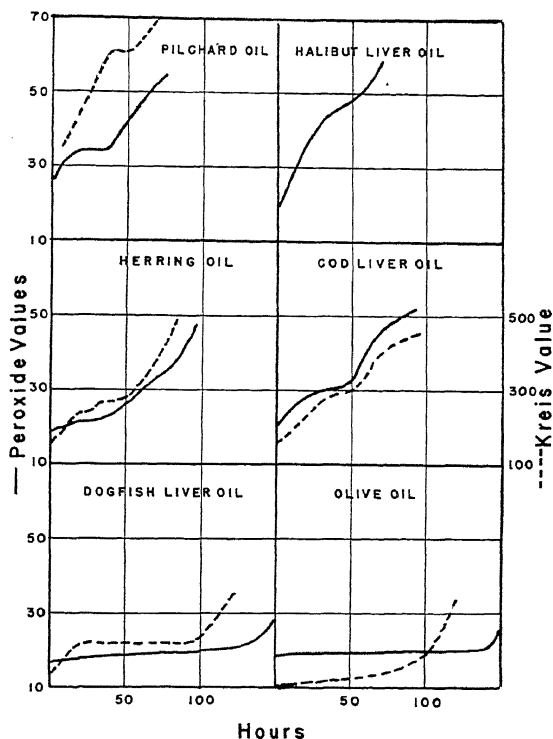
FIGURE 22. Development of rancidity in some fish oils as measured by peroxide and Kreis values.

In the majority of experiments carried out in these laboratories, the oxygen absorption test and the peroxide value have been found to be the most satisfactory. Since our oxygen absorption apparatus was designed to give the end of the induction period only, we have no data to show the full extent of the oxygen absorption reaction. However, from figure 22 it may be seen that the curve showing the progress of peroxide formation is roughly similar to the ordinary oxygen absorption curve, in that there is an initial period of more or less latent peroxide formation, which is analogous to the "induction" period of the oxygen absorption curve. For that reason the length of this period has been taken as the measure of the stability of the oil towards atmospheric oxidation in data given in table XXIV. This would appear, in the authors' opinion, to be the only

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accurate method of expressing stability towards oxidative rancidity in terms of peroxide content. The use of the period of time required to reach an arbitrary peroxide value, such as used by Green and Hilditch (1937), is justifiable only when working with a simple mixture of esters or fatty acids, as used by these authors, and can never be used in comparing different oils. Oils of the same initial peroxide level will often vary considerably in induction periods by the oxygen absorption test, as pointed out by French, Olcott and Mattill (1935). From table XXIV it will be seen that there is relatively good agreement between the stabilities as measured by those two tests. For this reason and also by reason of its reliable technique, the peroxide value is looked upon as being the most satisfactory of the chemical tests.

The Kreis value as used in these laboratories has proved quite unsatisfactory as an indicator of the onset of rancidification. As seen from figure 22, no definite relationship was obtained between peroxide values and the Kreis test. With increase of time of exposure, a yellow colour developed and increased constantly, making the red colour proportionately harder to read. This, along with the fact that the red colour levelled off after a certain—not very advanced—stage of rancidity had been reached, made the use of this test quite unreliable. A phenomenon of peculiar nature was the fact that an intense green colour was obtained with halibut liver oil when subjected to this test. Strangely, this was not true of all samples of halibut liver oil, some giving the ordinary red colour without the slightest trace of green. No satisfactory explanation can be given for this strange behaviour, unless it was due to contamination with metals such as copper or iron during production of the oil.

Of tremendous commercial importance is the fact that the ordinary acid, alkali and decolorizing processes to which many "refined" oils are subjected, have a drastic effect in accelerating the subsequent rate of atmospheric oxidation. Mattill and Crawford (1930) have shown that such treatments will shorten the induction period as much as five or six times for crude corn oil. Working with pilchard oil, Denstedt and Brocklesby (1936) showed the effect of treatment with decolorizing carbon and bleaching earth, and of acid and alkali washing on stability towards atmospheric oxidation. The data in figure 23 show that in every case these treatments considerably shortened the induction period of the oil. The experiment was not precise enough to establish which treatment rendered the oil most susceptible to oxidation. On keeping the oils for one month, it was found that the refined oils absorbed oxygen almost immediately upon being placed in the oxygen absorption apparatus, whereas the raw oil still exhibited a definite, although shorter, induction period.

This effect of the refining of oils has been ascribed by Holm, Greenbank and Deysher (1927) and their contemporaries to the removal of natural antioxidants, and this theory is now generally accepted. In the foregoing experiment, the refining treatment had apparently not been sufficient to remove all traces of such substances, and, as the samples slowly oxidized during storage, these antioxidants were broken down, and the susceptibility of the oils to oxidation was increased.

Not only are alkali and acid treatments conducive to such an acceleration in oxidation, but the ordinary commercial practices of expressing oils at relatively high temperatures shorten the induction periods considerably, as compared with solvent-extraction of oils. Cold-clearing of an oil also shortens the period of induction, but in this the effect may be attributed largely to the removal of the more saturated constituents of the oil, although there may be a simultaneous removal of the natural antioxidants to a certain extent. Decrease in susceptibility to atmospheric oxidation on decolorization by means of such agents as carbon and activated earths may be due not only to the direct removal of natural antioxidants, but also to the removal of pigments which ordinarily protect the oil from the accelerating influences of light. This effect has already been mentioned
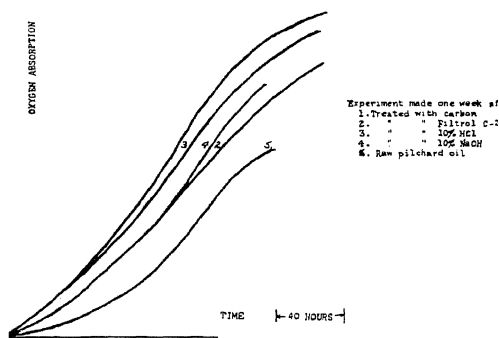
FIGURE 23.

in discussing the methylene blue reaction, and pertinent data are shown in table XXV. As acid treatments generally result in a slight decolorization of the oil, this effect may be accounted for partly by assuming partial association of the natural antioxidants with the pigments in the oil.

Since it is known that peroxides in oil serve to act as catalysts of further production of peroxides, the writers carried out an experiment to ascertain whether the removal of the initial peroxides would have any retarding effect on the subsequent rate of oxidation. This removal was effected by treating the oil with an acetic acid-chloroform mixture containing powdered zinc. In the presence of this mixture the oils were heated in an atmosphere of nitrogen on a hot water bath, until a negative test for peroxides was obtained. They were then washed free of acid with freshly boiled distilled water and dried over anhydrous sodium sulphate, the last traces of chloroform being removed by distillation. The whole operation was performed in an atmosphere of nitrogen.

Four samples of raw pilchard oil were taken, and of these three were treated as follows: (1) the peroxides removed, (2) refined with alkali, and (3) refined with alkali and the peroxides

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removed. All four samples were exposed for oxidation, and the development of subsequent oxidative rancidity was followed by the peroxide value.

The results obtained from this experiment are shown graphically in figure 24. Freeing the raw oil of initial peroxides has by far the most noticeable effect on subsequent oxidation, whilst such teatment of the alkali refined oil has no effect whatever. The only apparent explanation which may be offered is that the somewhat drastic acid treatment given the oils in order to remove initial peroxides may also destroy the natural antioxidants present and actually convert them into
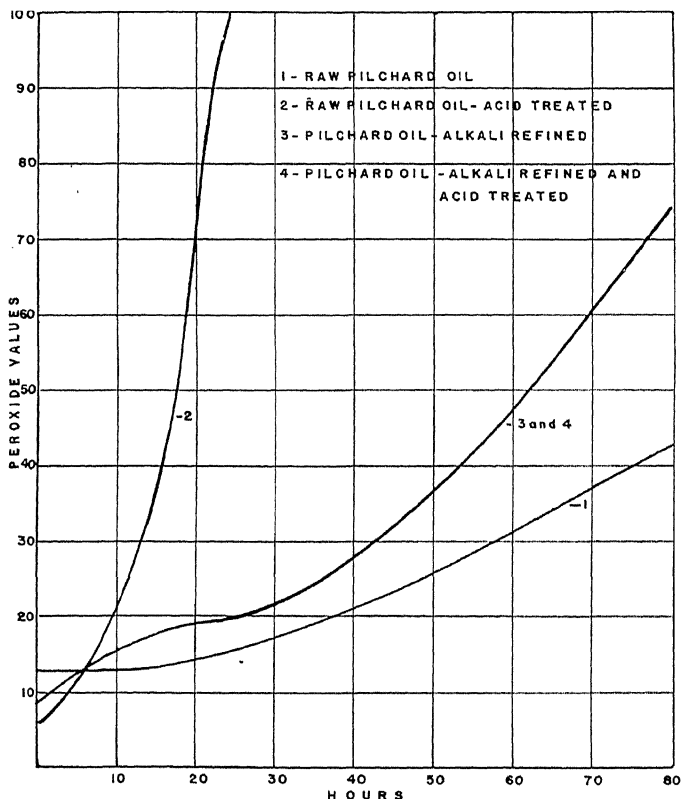
FIGURE 24. Effect of acid and alkali treatments on development of peroxide content of pilchard oil.

powerful pro-oxidants. In the case of the alkali-refined sample, the natural antioxidants are removed to begin with, so that no such action is possible. This, however, is merely an assumption, and requires further evidence for substantiation. Needless to say, the removal of the initial peroxides by any such method as this has, at present, no practical application.

Since it was desirable to know for commercial purposes whether the use of ordinary filter-aids (as distinct from activated earths) would have any detrimental effects on the keeping qualities

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of fish oils, four different samples of such aids were used with pilchard oil, and the course of subsequent oxidation followed by determining the peroxide values.

The samples were prepared by mixing two grams of filter-aid in 100 grams of oil, heating to 50°C. under an atmosphere of nitrogen, and filtering by suction while still warm. The control sample of raw oil was treated in a similar manner. The four samples of commercial filter-aid used were Filter-Cel, Celite, Super-Cel and Dicalite. The data are shown in figure 25.

In the results obtained, it is interesting to note that Filter-Cel, least purified of the filter-aids, had the smallest effect on susceptibility to oxidation, while all the other samples apparently tended to remove a certain amount of natural anti-oxidants from the oil, thus increasing the subsequent rate of oxidation. This is probably due to the fact that the active surface (with regard to the removal of natural antioxidants) of the particles of the more impure filter-aid would be considerably less than that of the others.
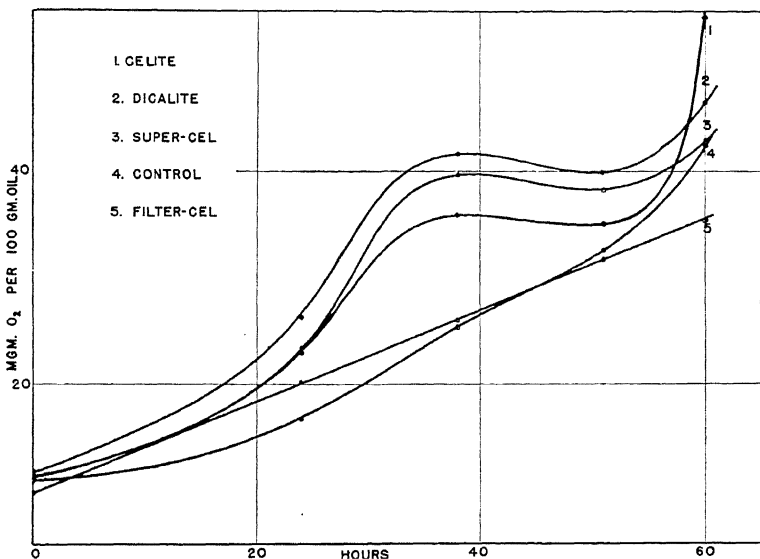
FIGURE 25. Effect of filter earths on development of peroxide content of pilchard oil.

From the foregoing discussion it may be readily seen that the commercial producer of fish oils cannot exercise too much care in controlling accurately the conditions of production and storage. Accelerating influences such as the action of light, metals and temperature must all be kept at a minimum and there should be resort to refining processes only when subsequent conditions of storage and marketing are to be rigorously guarded.

(d) EFFECT OF PEROXIDES ON VITAMIN A

It has been well established that oxidative rancidity in oils or fats destroys vitamin A (Fridericia 1924; Powick 1925; Mattill 1927; and others). The suscep-

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tibility of this vitamin to oxidation appears to be greater than that of some unsaturated fatty acids, since Monaghan and Schmitt (1932) showed that vitamin A in small concentrations may completely inhibit the oxygen uptake of linoleic acid for some hours. This inhibition wears off as the vitamin is destroyed by oxidation. Whipple (1936) found that the vitamin A in cod liver oil decreased as the peroxide value increased. The destruction of vitamin A per unit increase in peroxides was greater at 20°C. than at 100°C., showing that the mechanism of oxidation at these two temperatures must be different. Lowen, Anderson and Harrison (1937) have shown a relationship between peroxide formation and vitamin A destruction in halibut liver oil. Rapid destruction of vitamin A occur-
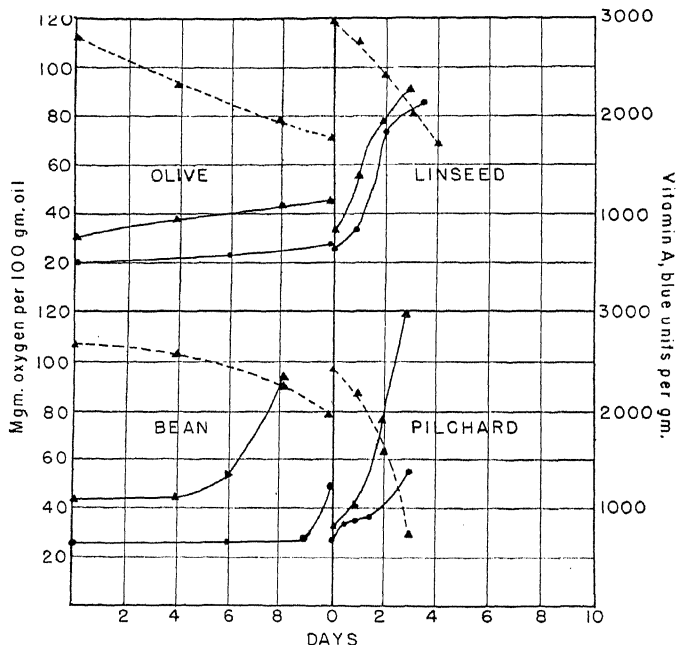
FIGURE 26. Relationship between peroxide content and deterioration of vitamin A. ● Raw oil, ▲ Raw oil plus vitamin A,—Peroxides ---- Vitamin A.

red when the end of the induction period (as indicated by peroxide value) was reached. These investigators found, however, that when oils were kept in stoppered bottles and exposed to diffuse daylight, no relation between peroxide formation and vitamin A destruction could be obtained. This observation coincides with that of Coe (1938), who claims that in rancidity due to light, organic peroxides do not seem to enter into the reaction.

Fish oils are by far the most important source of vitamin A, and, in addition, most of them are highly unsaturated and prone to undergo oxidative rancidity. As shown in a previous Section, susceptibility to oxidative rancidity is, in general,

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related to the gross unsaturation of the oil, and one would naturally expect that vitamin A in a highly unsaturated oil would be more unstable than in a less unsaturated one. Also, it might be expected that the peroxides in a highly unsaturated fatty acid molecule might decompose more readily than those of a less highly unsaturated acid, with the consequence that destruction of vitamin A might proceed more rapidly per unit weight of peroxide in highly unsaturated oils than in those of lower unsaturation. In view of the modern tendency towards concentration and blending of vitamin A oils, these factors have some practical value, and Brocklesby and Green (unpub.) carried out some experiments in an
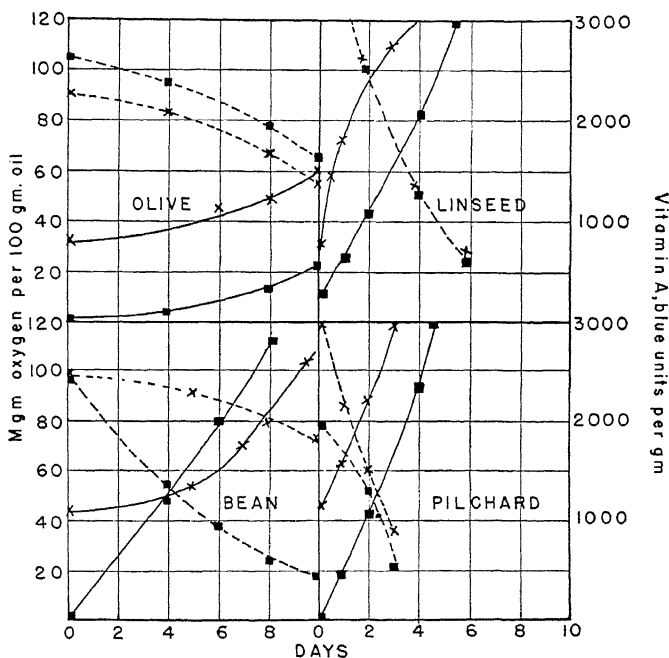
FIGURE 27. Relationship between peroxide content and deterioration of vitamin A. ×, alkali refined, ■, peroxide-free, ——, peroxides, ----, vitamin A.

effort to determine the relationship between peroxide formation, total unsaturation and vitamin A destruction.

In this work four oils representing increasing degrees of unsaturation were used, namely, olive, bean, linseed and pilchard oils. Peroxide formation and vitamin A destruction were followed in samples exposed in shallow petri dishes at 25°C. in a dark cabinet, in which a constant circulation of air was maintained. The peroxides were determined by Lea's method and vitamin A by the antimony trichloride method, using a photo-electric colorimeter. The oils were exposed in the cabinet in (1) the raw state and also after the following treatments; (2) raw oil plus one per cent unsaponifiable matter from halibut liver oil; (3) alkali-refined oil plus unsaponifiable matter; and (4) alkali-refined oil followed by treatment with acid and zinc to remove peroxides, and then plus unsaponifiable matter. The results, given in figures 26 and 27, show conclusively

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that the oxidation of vitamin A is closely related to peroxide content, and that this vitamin is more stable when dissolved in the less unsaturated oils such as olive and bean oils. In most cases the added unsaponifiable matter contained some peroxides. This additional quantity of peroxides seem to have no effect on the subsequent rate of oxidation of raw olive and linseed oils, but in the case of raw bean and pilchard oils the induction periods were considerably shortened.

In the raw oils to which halibut-liver-oil unsaponifiable matter had been added, the decrease in vitamin A per unit increase in peroxides was much greater for the olive than for the other three more highly unsaturated oils. This is undoubtedly due to the fact that in the highly unsaturated oils the rate of peroxide formation is more rapid than that of the oxidation of the vitamin A, and consequently the peroxides accumulate in tremendous excess. In the olive oil the rate of peroxide formation is slow and more comparable to that of the oxidation of vitamin A. It should be noted, however, that if peroxides are plotted against vitamin A content, olive oil gives a linear relationship through practically the whole course of the oxidation of vitamin A; linseed and pilchard oils give curves that are linear over the first part of the reaction, but slope off rapidly towards the end, indicating a more rapid destruction of vitamin A per unit increase of peroxides at the higher peroxide content levels. Bean oil gives curves intermediate between the above types, sometimes favouring the olive oil type and at other times the type given by the more highly unsaturated oils.

With olive oil, alkali-refining and acid removal of peroxides had much the same effect on the subsequent rate of peroxide formation and destruction of vitamin A. Both treatments, however, made the oil more susceptible to oxidation, but the rate of vitamin A destruction was approximately the same as that in the untreated raw oil. Alkali-refining of bean oil did not completely eliminate the induction period, but in this oil, subsequently acid treated to remove the peroxides, the induction period was completely eliminated with a consequently more rapid destruction of vitamin A. In linseed and pilchard oils, alkali-refining completely eliminated the induction period and in most cases the subsequent acid treatment had little further effect. In the case of the pilchard oil, however, the alkali-refined oil had a very high initial peroxide content, and the subsequent destruction of vitamin A was much more rapid than that taking place in the peroxide free oil.

These results emphasize the great danger of alkali or acid treatment of oils containing vitamin A unless such treated oils are protected with an antioxidant. They also show that where blending of high vitamin A oils is necessary, it is desirable to use oils of low unsaturation.

(e) ACTION OF ENZYMES

The two types of enzymes that may cause deteriorations in fats are the fat-splitting lipases and the oxidizing lipoxidases. Both are elaborated in the animal body and may be present in the oil or fat extracted from fish, unless certain precautions are taken. In the case of stored fatty fish, such enzymes undoubtedly play an important role in the keeping qualities, particularly with

respect to the stability of the accompanying fat. These enzymes are also produced by micro-organisms such as moulds and bacteria; indeed the action of micro-organisms is entirely due to the enzymes they secrete. There are thus two sources of fat-deteriorating enzymes, the animal body from which the fat or oil is produced and contaminating micro-organisms; the following discussion can therefore be considered from these two standpoints.

Of the two types of enzymes the lipases are probably the more important. In the animal organisms these are found in the greatest concentration in the digestive organs, but are also present in the muscle, blood and other tissues. The properties of the lipases differ somewhat with their source, but all are capable of splitting fats and oils into free fatty acids and glycerol. They are all inactivated by heat, the lethal temperature being in the vicinity of 100° C. Their activity decreases with decrease in temperature, but, even below the freezing point of the tissue, their activity, though slight, may be of some consequence over a long period of time. In general, the effect of naturally-occurring enzymes in cold-stored tissues is masked by the greater activity of the lipolytic enzymes produced by the bacteria. Indeed, in many products undergoing deterioration by the production of free fatty acids it is difficult to say which enzymes play the more important role, those in the tissues or those produced by the bacteria.

In fisheries products increase in free fatty acids of the oil may in some cases be directly attributed to the natural enzymes present in the tissues. The work of Drummond and Hilditch (1930) on the relationship between the time of storage of cod livers and the quality of the resulting oil is of importance in this connection, although (in the writers' opinion) possible bacterial effects cannot be ruled out entirely. Some of their data are given in table XXVI.

TABLE XXVI. Effect of time of storage of cod livers on quality of resulting oil
(Drummond and Hilditch 1930)

Approx. time of storage at 5°C. (hours)	Weight of livers (lb.)	Oil obtained			
		Weight (lb.)	Colour		Free fatty acids (%)
			Y	R	
0	24	5	2.2	0.3	0.07
5	14	4	2.3	0.1	0.10
24	14	3½	2.3	0.2	0.18
48	14	3½	3.0	0.4	0.30
72	14	1½	3.0	0.4	1.05
96	14	trace	8.5	0.8	1.50

These results indicate the marked increase in free fatty acids and colour with aging of the livers. They also indicate that, as the livers deteriorate, emulsification during steaming increases, with a resulting decrease in the yield of free oil. Further experiments by these authors involved (1) the use of anti-

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septics on the stored livers, which had no retarding effect on the rate of formation of the free fatty acids; and, finally, (2) the introduction of small pieces of variously treated liver material into medicinal cod liver oils that were stored for periods of time up to 13 months. The latter work showed fairly conclusively that the rapid formation of free fatty acids was due to the enzymes present in the livers themselves. These authors conclude that: "Deterioration of the livers, and hence of the technical quality of the oil is due to the retrogressive changes effected by the enzymes, etc., present within the liver tissue."

Similar results have been obtained in these laboratories during many investigations of halibut livers. It is well known that such livers, if not processed whilst still fresh, yield an oil that is very high in free fatty acids, or, if in the processing an alkali digestion is used, considerable amounts of soaps are formed. In one or two instances the writers have examined oils that had free fatty acid
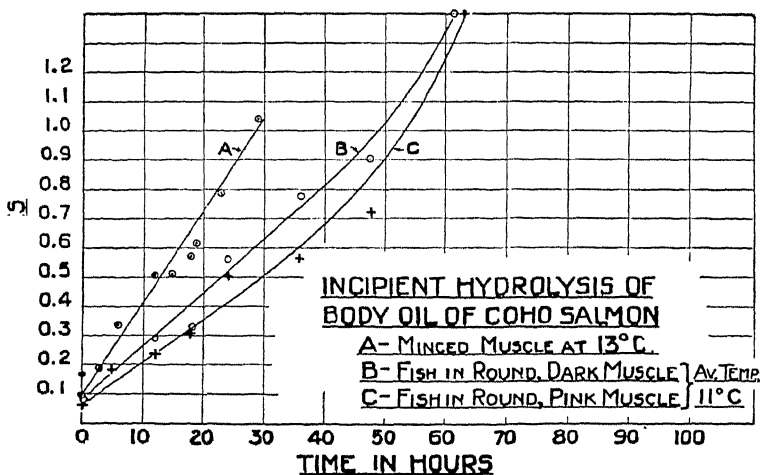
FIGURE 28.

values that indicated nearly 50 per cent hydrolysis. In some experiments carried out by one of us, in which various antiseptics were used to preserve the livers, no decrease in the rate of free fatty acid formation was observed, thus corroborating the view that the natural enzymes present in the liver tissue play the important role in the deterioration of liver oils.

The oil in the muscle tissue of fish also undergoes rapid enzymic hydrolysis. In figure 28 will be found data by Brocklesby (1933) showing the increase in free fatty acids of the oil of coho salmon, both in the minced condition and in fish kept in the "round." The minced tissue was kept at a slightly higher temperature than the fish in the "round," and this, plus the fact that bacterial contamination had undoubtedly taken place, probably accounts for the more rapid rate of hydrolysis. The fish in the "round" were gill-net caught fish which

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were stunned immediately after catching, and kept in an insulated hold without ice. The possibility of the hydrolysis being of bacterial origin is in this case more remote, and the results can be taken as indicating the very powerful effect of the naturally-occurring fat-splitting enzymes.

Results of the same sort have recently been obtained in these laboratories in connection with the effect of time and temperature of storage on the oil obtained from whole herring. The acid value of the oil from fresh herring was less than 0.1, whilst after 3 and 7 days at a temperature of 2°C. it was 0.2 and 1.0, and at a temperature of 15°C. it was 1.5 and 7.7, respectively.

The development of a high free-fatty-acid content in commercial fish liver and body oils through the action of tissue lipases usually takes place in the raw material before processing. Modern methods of production involve the use of temperatures of 100° C. or over, and the tissue lipases are therefore inactivated. Any subsequent development of free fatty acids will usually be found to be due to re-contamination by bacteria. This does not apply, however, to those methods which utilize low temperatures, i.e. so-called vacuum methods, and those involving the cold extraction of oil from frozen or mechanically "dehydrated" tissues. Oils produced by such methods should be heated at 100° C. in order to inactivate any accompanying enzymes.

It was stated previously that, even at temperatures below the freezing point of the tissue, enzymic splitting of fat may have some effect on the quality of the stored material. The evidence for this may now be examined. First let us consider some data obtained by Balls, Matlack and Tucker (1937), who worked with sterile mixtures of various fats, oils and the lipase from the pancreas. These investigators found that the smaller the fatty acid molecule in the fat or oil, the smaller was the retarding effect of lowering the temperature. In other words, at low temperatures, fats and oils containing small fatty acid molecules would undergo a more rapid enzyme splitting than those containing larger molecules of fatty acids. More important still to those interested in the stability of cold stored fish, was the discovery that unsaturated oils (i.e. oils usually liquid at room temperature), such as olive oil, behave in this respect like the fats containing fatty acids of small molecular weight. This means that the more liquid an oil is, the smaller will be the retarding effect of low temperatures on the action of lipases. Table XXVII contains data showing the relative lengths of time at various temperatures required to effect a hydrolysis of 5 per cent of olive oil by pancreatic lipase. No similar data are available for fish oils, but, since practically all fish oils are more highly unsaturated than olive oil, they will, in general, behave in a manner similar to that of the latter oil. Whilst

TABLE XXVII. Time estimated for 5 per cent splitting of olive oil by pancreatic lipase (Balls, Matlack and Tucker 1937)

Temperature (°C.).....	40	30	0	−6.7	−12	−30
" (°F.).....	104	86	32	20	10.4	−22
Time (days).........	0.0008	0.0016	0.06	0.25	0.9	7.2

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the time required to effect a definite amount of hydrolysis appears to increase rapidly with decrease in temperature, a little reflection will show that, even at −30° C. (−22° F.), the rate of hydrolysis is still a matter of commercial importance. At this temperature the same amount of hydrolysis will be effected in about 4 months' time, as that in 1 day at 0° C. (32° F.). Four months is not an unusual storage period, but a storage temperature of −30° C. is still the exception rather than the rule.

TABLE XXVIII. Development of free fatty acids in oil of red spring salmon held in commercial cold storage for various times.

Time (weeks)	Acid value of oil	
	Pink muscle	Dark muscle
1	1.03	0.67
7	3.06	2.50
16	5.52	4.18
52	14.4	12.6

In the light of the above, data obtained by Brocklesby (1933) on the increase in free fatty acids of the oil of stored frozen salmon are of some interest here. Table XXVIII shows the increase in free fatty acids of the oil extracted from the deep lateral (pink) muscle and the superficial lateral (dark) muscle of red spring salmon held in commercial cold storage at an average temperature of −13° C. (8.6° F.). The development of free fatty acids was rapid, and of an order definitely detrimental to the quality of the stored product. The difference between the free fatty acids from the deep pink muscle and from the superficial dark muscle is interpreted as meaning a greater concentration of enzymes in the deep muscle than in the superficial. Another more serious interpretation is discussed in a later section of this Bulletin when the secondary effects of free fatty acids in fisheries products are considered. The data given here are sufficient to emphasize the need for proper storage temperatures for goods susceptible to enzyme hydrolysis.

(f) ACTION OF MICRO-ORGANISMS

The action of micro-organisms is due to the enzymes they secrete. To a large extent selective action of such organisms is the result of the elaboration of specific "constitutive" enzymes, which are always produced by a given organism irrespective of the nature of the medium on which it is grown. Some species can also modify their nutritional requirements by the production of "adaptive" enzymes, which appear in the organism when a certain constituent is present in the medium. Thus a particular micro-organism can be said to elaborate a specific group of enzymes and also, when the necessity arises, other groups of enzymes that will allow the organism to cope with the change in the food on

which it is growing. Adaptation by micro-organisms, however, appears to be limited, and thus we find bacteria that will attack proteins but not carbohydrates or fats, and others that can act on carbohydrates but not on proteins. In the present connection we are interested in those organisms that can act on fats or oils through the medium of lipases or lipoxidases, but we shall also have to consider briefly those organisms that act on proteins, because many of the products of protein decomposition are soluble in fats or oils.

For growth, micro-organisms require sources of carbon, nitrogen, inorganic salts and moisture. In addition, the physical nature of the environment is important. As far as temperature is concerned, the range over which micro-organisms can grow, extends from about $-7.5°$ C. (18.5° F.) to about 60° C. (140° F.). Above this temperature most organisms are killed. The range of optimum growth varies, but would appear to be between 20° C. (68° F.) and 37° C. (98.6° F.). Below $-7.5°$ C. micro-organisms are not necessarily killed, many kinds of bacteria for instance surviving temperatures as low as $-70°$ C. ($-94°$ F.), but the lower the temperature the higher the mortality. Moulds and yeasts are more adaptive than bacteria, and can flourish in more acid media and at higher salt concentrations. Bacteria are more sensitive to low atmospheric humidities than either yeasts or moulds, but, if the material on which they are growing contains much water, humidity has little effect on any of them, since moisture evaporated at the surface can be quickly replaced. On the other hand, moulds and yeasts are more susceptible than bacteria to carbon dioxide in the atmosphere, and storage in this gas has proven to be advantageous in the case of certain fatty foodstuffs.

Fat-splitting lipases have been shown to be produced by a large number of bacteria and moulds and a few yeasts. Bacteria and moulds cause the development of free fatty acids in stored fatty products such as meats, poultry and fish, both in the presence and in the absence of oxygen. The lipases produced by these organisms do not always remain within the cell structure of the organism, but often diffuse into the surrounding tissue and cause extensive formation of free fatty acids. Fully saturated fats appear to be acted upon by bacteria only with difficulty, but unsaturated liquid fats are readily attacked. As mentioned earlier, development of free fatty acids does not necessarily mean that a fat or oil has become rancid, but it is the opinion of some investigators that spoilage by micro-organisms is always preceded by free fatty acid formation.

Relatively little information is available regarding the formation of lipoxidases by micro-organisms, but a recent experiment described by Jensen and Grettie (1937) shows definitely that organisms that produce lipoxidases are able to cause rancidity in oils and fats. These workers inoculated a leaf-lard and a hydrogenated cottonseed oil shortening with organisms that produced lipase (Culture 3), lipoxidase (Culture 48), and both enzymes together (Culture 14). After incubation at 37°C. for a period of 14 days, the various samples were examined by seven different methods. Jensen and Grettie concluded from the results of this experiment that "micro-organisms may induce: (1) oxidative rancidity (Culture 14); (2) hydrolysis with high free fatty acids (lipase-former Culture 3); tallowiness (oxidizers) in beef fat, mutton fat, and leaf lard (Culture 48 and other experiments); in addition, wherever oxidizing types of microbes exert their influence, flavour changes take place—some changes are 'flavour reversions' such as one finds in deodorized oils and

fats, and some are 'flavour adjuvants' in which condition the flavour is reinforced and also altered in character."

The combined production of lipases and lipoxidases by micro-organisms can thus bring about a rancid condition in fats and oils. In medicinal and industrial fish oils this type of spoilage should not be a serious matter, since it has been shown by Jensen and Grettie that moisture-free fats do not support the growth of micro-organism, but that 0.3 per cent moisture or more aids in promoting their growth. The lipase- and lipoxidase-forming micro-organisms are more likely to damage the oil when in the tissue than after it has been extracted.

In addition to those organisms that actually attack fats and oils, those that act on proteins are also capable of causing spoilage of fats. Among the products of the metabolism of putrefactive bacteria are many odorous substances such as amines, skatole and indole, low molecular-weight fatty acids, alcohols and hydrocarbons. Many of these substances are soluble in oils and fats, and will spoil an otherwise high-grade product by the odour which they confer on it. This kind of spoilage is probably more widespread in the fishing industry than is generally recognized. It is an insidious type of spoilage, but in some cases can be partly controlled or entirely eliminated.

A complete description of methods for the control of micro-organisms is beyond the scope of the present Bulletin, but a few general principles, together with some experimental details, may be given here. Deterioration in the quality of medicinal and industrial fish oils by the action of micro-organisms can take place (1) in the material before processing, (2) during processing due to unclean plant equipment, (3) during processing through faulty technique and (4) through failure to produce a "clean" dry oil. Where the raw material is processed on a large-tonnage basis, economical treatment for the control of bacterial spoilage is very difficult. The material should, of course, be held at the lowest possible temperature. In the case of material that decomposes very rapidly, such as waste from salmon canneries, some consideration should be given to spraying with a bactericidal material such as dilute formaldehyde. Mixtures of aldehydes are now commercially available for this purpose, and they all have the advantage of not remaining as aldehydes in the finished fish meal. That which does not combine with the protein is volatilized during processing. As far as the writers are aware, such aldehydes at the concentrations used do not affect the quality of industrial oils.

The preservation of livers or intestines of fish is a more serious matter since in this case the object is the production of a vitamin-containing oil of high quality for medicinal use. As this material is more valuable than the raw material in bulk, discussed above, more elaborate precautions can be taken to preserve it from putrefactive decomposition. Up to the time of landing in port, ice has been the *sole* means of preservation, but judging from the condition of certain parcels of livers examined by the writers, this leaves something to be desired. In seeking a preservative for livers or intestines, three important criteria must

be kept in mind, namely the effect on (1) bacterial decomposition, (2) subsequent oil recovery and (3) the vitamin potency of the preserved material. In addition, the solubility of the preservative in the oil with possible subsequent physiological effects must be considered. With these criteria as limiting factors, Brocklesby and Green (unpub.) examined a number of substances that appeared to have some merit as preservatives. From a preliminary experiment with 12 substances, 6 were chosen for a seven-day incubation test with macerated fresh halibut liver. Total volatile nitrogen was used as an indicator of bacterial decomposition. Table XXIX shows the results of this experiment.

TABLE XXIX. Effect of various preservatives on total volatile nitrogen in halibut livers.

Substance	Concentration (%)	Total volatile nitrogen (mg. per 100 g.)
Control		731
Borax	0.5	642
	1.0	230
	2.0	88
Salicylic acid	0.05	718
	0.10	748
	0.20	212
Boric acid	1.0	306
	2.0	225
	5.0	220
Sodium chloride	8.0	278
	15.0	146
	25.0	164
Acetic acid	1.0	215
	2.5	360
	5.0	308
Formalin	0.5	270
	2.5	80
	5.0	88

All the preservatives had some inhibiting effect on the bacterial production of volatile nitrogen. Of these six substances, three were chosen for further work on the effect of processing and vitamin A potency, with the following results:

Borax, at a concentration of 2 per cent, kept halibut livers or intestines fairly free from bacterial decomposition for a period of a week at room temperature. During this time, however, considerable autolysis took place and in addition there appeared to be some saponification of the oil. The livers and intestines quickly lost their identity and became very soft. The borax did not appear to have any effect on either pepsin or alkali digestion of the livers or intestines, with the exception of the emulsification due to the excessive soap formation. During a storage period of ten days the borax caused little, if any, loss in vitamin A potency.

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Salt, at a concentration of 10 per cent, preserved and dehydrated both the livers and intestines. They therefore retained their shape and identity. The proteins of both the livers and intestines were much more difficult to digest by the pepsin and alkali methods than those of the controls. Lower oil yields were therefore obtained, but the vitamin A potency was not affected.

Formalin, at a concentration of 0.25 per cent, caused an immediate coagulation of water-soluble proteins with the consequence that the livers and intestines formed a solid mass, in which it was difficult to distinguish individual organs. After two weeks at room temperature, both the liver and intestines were still fresh. No difficulty was encountered during pepsin or alkali digestion of either material, and good oil yields were obtained. During preliminary experiments, no loss in vitamin A potency was noticed in the formaldehyde treated material, but in several subsequent experiments rather serious losses were observed. These discordant results have not as yet been explained, but further experimental work is being carried out.

One commercial company has done considerable experimental work in connection with the preservation of fish livers and intestines, and, as a result, has put on the market a preservative consisting of a mixture of salts, which at a concentration of 10 per cent, will, it is claimed, preserve livers and intestines for a period of months with no putrefaction and no loss of vitamin A. The results of large scale experiments with this material on cod, dogfish, tuna and halibut livers have been very promising and the use of such a preservative would appear to be of definite benefit in producing medicinal oils of high quality.

Spoilage of oil due to unclean plant equipment is not as prevalent a cause as it was a few years ago. It is now customary to "hose" and "steam down" all run-ways and machinery, but more care still should be exercised in cleaning settling and storage tanks. The stick-water from the presses contains dissolved protein that is an excellent medium for the growth of all kinds of bacteria. Usually the tank becomes coated with a ring of semi-dried protein and oil, and, although the tank is periodically heated to effect the "break" of the oil, sterilization of the contaminating bacteria is never complete. Some time ago one of the writers examined such an encrustation and found that the oil in it had a very high acid value, a very foul odour, and, worst of all, a high content of peroxides. Unclean settling and storage tanks mean that extra contamination with bacteria is being provided. A periodic clean-out followed by spraying with a good commercial disinfectant would in many cases be an economic precaution.

Faulty technique during processing may also allow micro-organisms to damage an oil. This takes place chiefly during the separation of the oil from the stick-water. If the oil does not break readily it is the usual practice to keep the mixture hot until it does break. Salt is sometimes added, but with doubtful advantage. In modern plants the temperature is maintained almost at the boiling point, and bacterial action under these conditions is inhibited. But in many cases such a high temperature is not reached and nothing like a complete sterilization is obtained. The oil with the poor "break" is then run into the first settling tank along with an excess of water and protein material. Here the mixture cools, bacterial action commences, and, by the time the oil reaches the last tank in the settling system, it has a disagreeable odour and a higher free-fatty-acid content than it had when leaving the presses. Owing to variations in

the raw material, quick "breaks" in the settling tanks are not always easy to obtain, but failing the quick removal of the protein-containing water, the temperature of the mixture should be maintained as near to the boiling point as possible in order to inhibit bacterial growth.

An improperly settled oil usually contains an excess of moisture, containing dissolved or dispersed protein. In most cases sterilization is not complete, with the result that the oil "ferments". Odorous substances from the putrefying protein dissolve in the oil, and basic ammoniacal products are formed which unite with the free fatty acids to form a soap. Under these conditions further settling of the oil is practically impossible as the soap stabilizes the dispersed protein. It is impracticable to remove the odour from these kinds of oil and their use for many industrial purposes is restricted. Clarification of oils will be discussed further in Section 8, II (Processing).

II. STABILIZATION

The stabilization of oils and fats towards rancidity, particularly that due to atmospheric oxidation, has been one of the main problems of producers of shortenings and other fatty food products for the past quarter of a century. Many methods have been used, which may be summarized under four headings: partial hydrogenation, natural and chemical antioxidants and the use of physical methods such as protection from light, storage in inert gases, etc. The subject, therefore, is best treated under these headings.

(a) PARTIAL HYDROGENATION

In general, the more highly unsaturated the component acids of an oil, the more susceptible will the oil be to oxidative rancidity. Consequently, partial reduction of such highly unsaturated acids by selective hydrogenation will increase the stability of the oil towards oxidation. Waterman, van Vlodrop and Pezy (1936) have found that by using a partial hydrogenation process in the presence of a colloidal nickel catalyst, the stability of cod liver oil can be considerably increased without seriously affecting its physical properties or vitamin content. This is true for any oil where the proportion of the most highly unsaturated fatty acids is small, since these are the first to be reduced in the process of hydrogenation. Their partial saturation has a tremendous effect on the rate of atmospheric oxidation, but little relative effect on the properties of the oil. Partially hydrogenated oils are also claimed to be of greater nutritive value, owing not only to increased stability, but to the elimination of certain toxic substances during purification and hydrogenation (Ueno and co-workers, 1927). Beneficial effects on the stabilization of herring and sardine oils have likewise been reported by Ueno and Hayashi (1937). The partial saturation of oils by selective hydrogenation as a means of stabilization shows considerable promise.

(b) Natural Antioxidants

In the first part of this section, reference has been made to the presence of natural antioxidants in fats and oils which inhibit the initial atmospheric oxidation of the oils themselves. From the results of numerous investigations, almost conclusive evidence is offered as to the presence of such substances in freshly produced, unrefined oils. French, Hamilton, Olcott, and their co-workers (1934-1937) call these substances "inhibitols" to indicate the inhibiting action on oxidation, and also on account of the hydroxyl group which was found to be present in all such substances. Hilditch, Banks and their colleagues (1932-1939) have carried out extensive investigations as to the nature of these natural antioxidants, and find that they are invariably of a basic nature, and consist of basic oxygen rather than basic nitrogen compounds.

The presence of such substances in fish oils is well borne out in the effect of alkali-refining, acid treatment, etc., as described under atmospheric oxidation of these oils. No data are available as to their specific nature, but there is good reason to assume that they are similar to those occurring in vegetable oils. Practically identical results were obtained by Hilditch and Sleightholme (1932) by subjecting olive and codling liver oils to alkali and acid treatments. The proportion of natural antioxidants present in various fish oils probably varies considerably, which, with the widely differing degrees of unsaturation, accounts for the variation in stabilities of fish oils. Not only may the keeping qualities of fats and oils be improved by the retention of natural antioxidants, but also by the addition of such substances derived from other sources. Thus Mattill and Crawford (1930) stabilized corn oil by the use of the unsaponifiable fraction of wheat-germ oil. Numerous investigators have shown that seeds of plants contain relatively large amounts of natural antioxidants, which is to be expected, when one considers the much greater stability of the oil in seeds than of that in other parts of the plant. It has also been shown that natural antioxidants are associated with characteristic pigments in plants, while some investigators have found antioxidative properties in cereal flours when directly infused in the the oil, or used in wrapping materials.

Hilditch and his co-workers made some interesting observations as to the antioxidative properties of various seed extracts, particularly those from linseed and soya bean press cakes. After extracting the meal with 5 per cent acetic acid in water or acetone, they re-extracted the dried meal with methyl alcohol. The acetone-soluble portion of the latter extract gave the greatest antioxidative protection to freshly distilled esters of olive oil fatty acids. Olcovitch and Mattill (1931) isolated a crystalline compound from lettuce with strong antioxidative properties, and Bradway and Mattill (1934) obtained concentrates from the seed fats of tomatoes and carrots with similar properties.

In view of the strong antioxidative qualities exhibited by most of these substances towards oils of a fairly high degree of unsaturation, a number of seed extracts have been examined in these laboratories in the search for a suitable antioxidant for fish oils. The seeds were finely ground and extracted with

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petroleum spirits. In a preliminary experiment the extracted seeds were directly infused in herring oil by heating at 100° C. for 15 minutes in an atmosphere of nitrogen. The protective action of these infusions on herring oil is shown in table XXX. Very little effect was observed, but it is worthy of note that those seeds proving most effective by the infusion method were later found in practically all cases to give the most active extracts.

TABLE XXX. Antioxidative effect of various seeds (extracted with petroleum spirits)

Seed	P.F.*	Seed	P.F.*	Seed	P.F.*
Whole wheat........	1	Linseed...........	1.4	Pumpkin..........	1
Oats..............	1.1	Carrot............	1	Peanut (inner seed	
Hemp.............	1.1	Soya bean meal.....	1.4	coatings) in halibut	
		Peanut (whole seed) .	1.2	liver oil..........	1.6

$$*P.F. = \text{Protective factor} = \frac{\text{Induction period of oil} + \text{antioxidant}}{\text{Induction period of untreated oil}}$$

The methods used in extracting the seeds were the same as those of Green and Hilditch (1937). Details may be obtained from their paper, but are briefly summarized as follows:

Extract no. 1. One hundred grams of extracted seed were refluxed in 250 cc. of 5 per cent acetic acid in acetone for three hours. Filtered while hot and the solvent evaporated, the residue was stored in a desiccator in the presence of alkali. This was then dissolved in the oil by heating at 60°C. in the presence of nitrogen.

Extract no. 2. The seed from the previous extract was dried in a vacuum oven and then refluxed for one hour with 500 cc. of methyl alcohol. The hot filtrate was mixed with seven times its volume of cold acetone. After standing for 24 hours, the solution was filtered and the acetone evaporated. The residue after evaporation was stored in the same way as extract no. 1, and dissolved in the oil by heating at 100°C. in an atmosphere of nitrogen.

These extracts were tested on herring oil and halibut liver oil at various concentrations by the oxygen absorption method at a temperature of 50°C. The results are given in table XXXI.

While the protective action of these extracts was not as great on herring oil and halibut liver oil as is usually found on oils of lesser unsaturation, nevertheless there were indications of some activity at relatively high concentrations. At 5 per cent concentration, acetone extracts of wheat germ and carrot seed are quite satisfactory, but unfortunately such a high percentage would increase the unsaponifiable fraction in most commercial oils to too high a level. If the antioxidative constituents of these extracts can be further concentrated, the effective concentration can be further decreased, so that there will be no interference with the required chemical properties of the oil. The desirable feature of these extracts is that at concentrations of 1 per cent or lower, they do not impart any toxic properties, undesirable odour or taste to the oil. It should be noted that the protective factors in the above table were determined at 50° C. In actual practice, such high temperatures are never encountered during the storage or transport of an oil, and at lower temperatures the protective factor could be expected to be much larger. For instance, extract no. 2 of the inner coatings of peanuts gave a protective factor of 6.5 at a concentration of 1 per cent in halibut liver oil at 27° C.

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TABLE XXXI. Antioxidative effect of various seed extracts.

Oil	Seed	Extract (No.)	Concentration (%)	P.F.
Herring	Soya bean	1	5.0	2.4
"	" "	2	1.0	1.2
"	" "	2	2.5	2.0
"	Wheat germ	1	0.2	1.4
"	" "	1	2.0	2.5
"	" "	1	5.0	4.0
"	Dockage	1	2.0	2.0
"	"	1	5.0	2.5
"	"	2	0.5	1.4
"	Carrot	1	0.5	1.2
"	"	1	1.0	1.5
"	"	1	2.0	2.4
"	"	1	5.0	5.0
Halibut liver	Carrot	1	0.5	1.1
" "	Dockage	1	0.5	1.2
" "	Celery	1	0.5	1.6
" "	Wheat germ	2	0.5	1.5
" "	Tomato	2	0.5	1.1
" "	Sunflower	2	0.5	1.4
" "	Barley	2	1.0	1.6
" "	Peanut (inner coatings)	2	1.0	2.2
" "	Lettuce	1 & 2	1.0	2.1

Antioxidative properties have been ascribed to carotene and lecithin by some workers, while others fail to find any such effect. Bradway and Mattill (1934) have explained this conflicting nature of carotene as an antioxidant by stating that crude carotene as separated from plant sources usually shows protective properties, owing to traces of contaminating substances which are powerful antioxidants. Purified carotene in some cases acts as a pro-oxidant. The same has been proved to be true for lecithin by the work of Olcott and Mattill (1936). Utilizing both these substances in experiments in these laboratories no beneficial effects were imparted to herring oil. Both crude and purified carotene and lecithin were used; the superior qualities of the crude material in preference to the purified material as an antioxidant were evident.

Another natural substance tested for its antioxidative influence towards fish oils was gum guaiac which is a good antioxidant in baked fat-containing foods. No such effects were evident in its action on fish oil; in fact in some cases it actually accelerated the rate of oxidation of the oils.

At the present time perhaps the most widely known natural antioxidants for fatty foodstuffs are the cereal flours, as they are non-toxic by nature and easily applied. Oat flour and soya bean flour are the most common and have been the subjects of many patents. In 1937, Lowen, Anderson and Harrison reported the effect of oat flour on the keeping qualities of halibut liver and

salmon oils. Little, if any, effect was noticeable for halibut liver oil and the rate of deterioration of vitamin A was quite unchanged. Some slight retarding effect on the rate of oxidation of salmon oil was apparent. As a preservative for halibut livers it showed favourable results, except that it interfered with the method of extraction used.

Both oat flour and soya bean flour were examined in these laboratories as to their effect on the development of rancidity. No activity was evident except at concentrations of 10 per cent and even then it was only slight. In figure 29
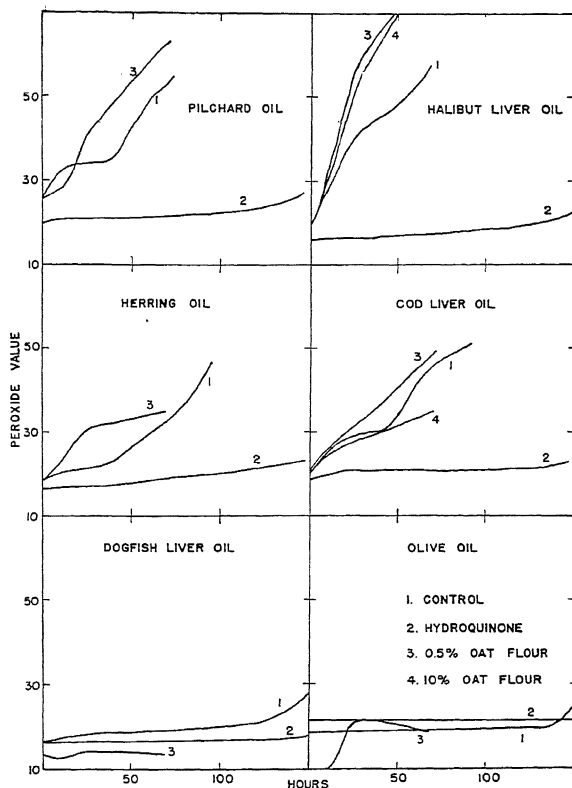
FIGURE 29.   Effect of some antioxidants on development of rancidity in fish oils.

are shown the curves obtained by using 0.5 per cent and 10 per cent oat flour in halibut and cod liver oils and following the course of oxidation by determining the peroxide values.

For halibut liver, pilchard and herring oils, the flour apparently acted as a pro-oxidant. In cod liver oil there was a retarding effect on oxidation at a high concentration, but it was not outstanding. There was no effect on the rate of deterioration of vitamin A in either halibut or cod liver oils.

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(c) CHEMICAL ANTIOXIDANTS

It has long been known that the addition of chemical substances of strong antioxidative properties will stabilize refined oils, and prolong the stability of unrefined oils. Such substances have been the subject of voluminous research. The majority of these investigations has been in the field of edible fats and fatty foodstuffs, such as lard, shortenings and vegetable oils. What little work has been done on fish oils and similar oils has only served to show that, as with natural antioxidants, many chemical antioxidants which exert powerful stabilizing influences on vegetable oils have little or no effect on fish oils. This fact, and also the suspected toxicity of certain powerful chemical antioxidants (which prevents their use in edible products) limits the number of possible materials that may be used. Considerable data have been obtained in these laboratories as to suitable chemical antioxidants for fish oils, and specific attention will be paid to this phase of the problem in the succeeding paragraphs. For the purpose of simplicity the various antioxidants are considered under the headings: phenolic inhibitors, amines and related substances, and acid-type inhibitors.

(i) PHENOLIC INHIBITORS

The use of such substances to stabilize oils and fats dates back many years. It is reported that the American Indians used tree bark (containing phenolic compounds) to retard the development of rancidity in bear grease. Mattill (1931) and Olcott (1934) have investigated the relative efficiencies of phenolic substances with the results shown in figure 30. It is interesting to note that a single hydroxyl group substituted in the benzene nucleus gives a substance (phenol) with no antioxidative properties. The addition of a second hydroxyl group enormously increases the activity when the hydroxyl groups are in the 1:2 or 1:4 positions. Resorcinol, with the hydroxyl groups in the 1:3 positions, is only slightly active. There is a further increase in activity with three hydroxyl groups. In this case pyrogallol (1:2:3) and hydroxyhydroquinone (1:2:4) are very much more active than phloroglucinol with the hydroxyl groups in the 1:3:5 positions. The addition of a fourth hydroxyl group considerably diminishes the activity. Direct substitution in the benzene nucleus is necessary for antioxidative activity; compounds with the hydroxyl group in the side chain are inactive.

Of all the phenolic compounds possessing antioxidative activity, hydroquinone has achieved the widest attention, particularly in highly unsaturated oils. With fish oils it was found to be far superior to any other chemical antioxidants studied. Holmes, Corbet and Hartzler (1936) found that a concentration of 0.1 per cent almost doubled the inductive period of halibut liver oil, and increasing concentrations resulted in still further stabilization against both oxidation and loss of vitamin A. With cod liver oil it gave a somewhat similar effect, except that a concentration of 0.2 per cent gave a maximum protective factor; subsequent increase resulted in decreased protection. In figure 29 are shown data obtained by using 0.1 per cent hydroquinone in the six oils tested in these laboratories during work on rancidification. Measured in terms of peroxide value, excel-

lent protection against atmospheric oxidation is evident for all six oils. This effect was particularly noticeable in the case of halibut liver oil, giving a protective factor of 5 by the oxygen absorption method, while a relative preservation of vitamin A potency was obtained.

The excellent antioxidative properties of hydroquinone and related substances, however, do not solve the problem of the stabilizing of fish oils destined for edible consumption, since the pure food laws of various countries disallow the use of such substances in edible products. No definite evidence is available as to the toxicity of hydroquinone; in fact, Olcovitch and Mattill (1931) found that doses sufficiently strong to stabilize fat-containing diets, fed to rats over considerable periods, had no injurious effects. However, in absence of more conclusive evidence, hydroquinone cannot be used as an antioxidant for edible fish oils.
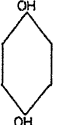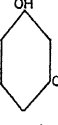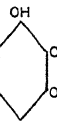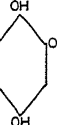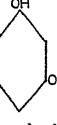
Monohydroxybenzene	Dihydroxybenzene	Trihydroxybenzene	Tetrahydroxybenzene

FIGURE 30. Antioxidative properties of phenols.

A number of patents have been taken out for more complicated phenolic compounds as suitable antioxidants, such as para-hydroxydiphenylmethane and various perfumes. Protection may be derived from phenolic compounds in wood, as shown by Takahashi and Masuda (1938), who found smoked herring oil to be much more stable than fresh herring oil, while even the passing of wood smoke through fresh herring oil slightly improved its keeping qualities.

(ii) AMINES

After the phenolic compounds, the aromatic amino compounds probably rank next in importance as antioxidative substances. The activity of the amines increases up to the secondary forms; primary, tertiary and quaternary have but slight activity. Working with linseed oil, Wagner and Brier (1931) found that

meta- and para-phenylenediamine in their ordinary forms gave no antioxidative effect; it was only when some spontaneous reaction had taken place (they heated the oil to 100°C.) that these substances proved to be stabilizing agents. These authors concluded that it was the decomposition products which exercised antioxidative influence.

Amines are used chiefly as antioxidants in the rubber industry. They are not used to any great extent in edible fat preservation, due to their reported toxicity. Glycine, an amino acid, was used in experimental work in these laboratories, but failed to impart any antioxidative properties whatever to the oils used. Other amino acids, such as glutamic and aspartic acids, have been reported by Lea (1936) and other workers to have strong antioxidative properties when used in lard, but for oils of greater unsaturation, the effect is no longer noticeable.

(iii) ACID TYPE INHIBITORS

Olcott and Mattill (1936) have shown that various inorganic and organic acids have definite antioxidative effects on the esters of hydrogenated cottonseed oil. They used a concentration of 0.02% in all cases and obtained the results shown in table XXXII.

TABLE XXXII. Antioxidative effect of certain acidic compounds on esters of hydrogenated cottonseed oil (Olcott and Mattill 1936)

Acid	P.F.	Acid	P.F.
Sulphuric (95%).............	15–20	Tartaric....................	10–15
Phosphoric (85%)...........	15–20	Maleic.....................	4–6
Perchloric.................	3	Malic......................	8–12
Arsenic....................	3	Pyruvic....................	10–15
Oxalic.....................	15–20	Citric.....................	10–15
Malonic...................	10–15		

Experiments with the esters of lard gave results of the same nature. The relative efficiencies of these acids as antioxidants are controversial, since practically every investigator reports a different order of effectiveness. This again is apparently due to the different types of fats used, but the general conclusion appears to be that acid-type inhibitors rapidly lose their efficiency as the unsaturation of the fats is increased.

(d) PHYSICAL AIDS

In the first part of this Section there was considerable discussion as to the effect of light and of dissolved oxygen and peroxides on the development of oxidative rancidity. Thus physical aids, such as the use of coloured wrappers that cut out the most active accelerating rays, and storage under inert gases, will result in some improvement in the keeping qualities of the oil. Protective coloured wrappers, in particular, have achieved considerable commercial importance, and are today being used extensively in packaging fat-containing products, medi-

cinal cod and other fish liver oils and vitamin concentrates, while storage at reduced pressures and in inert gases is also becoming more common, such as in the so-called "vacuum-packed" milk, coffee, etc., and cod liver oil saturated with carbon dioxide.

Numerous investigations have shown that the invisible ultraviolet rays are the most active in accelerating atmospheric oxidation, whilst in the visible spectrum the blue light of wave lengths shorter than 5,000 Å is most active. It has been found that coloured wrappers that exclude all light below 5,000 Å afford the greatest measure of protection. Yellow, brown or red are the most suitable colours for protective wrappers, yellow being most acceptable in that it transmits the greatest proportion of non-active light rays and alters to only a slight extent the transmitted colour of the contents of the package. According to Davies (1934, 1937) blue and green wrappers can be used if they are deeply coloured.

The use of protective wrappers for medicinal fish liver oils or for products containing fish oils results in a certain protection against oxidative rancidity, but it must be pointed out that the same care is still necessary in the preparation of the product, for if partial oxidation has proceeded in the oil, rancidity will develop irrespective of any wrappers used.

Considerable importance has been attached to the storage of oils in inert gases as a means of retarding oxidative rancidity. Nitrogen, hydrogen and carbon dioxide have generally been used for this purpose. Working with cod liver oil, Drummond and Hilditch (1930) found, however, that "neither nitrogen nor carbon dioxide are of any great service in excluding oxygen from entering into combination with the oil." They stored cod liver oil in 12½-gallon tins fitted with gas-tight caps. A gallon of oil was removed and the space filled with the gas under examination. Samples of the gas in this head-space were taken at regular intervals, and the analysis showed that the ordinary practice of filling this space by bubbling in gas for a few minutes did not cause sufficient displacement of air to materially retard oxidation.

Most commercial oils have sufficient dissolved oxygen in them to cause some oxidation, and the removal of such dissolved oxygen can only be satisfactorily accomplished either by steaming the oil or de-gassing under prolonged low pressures. The work of Holm, Greenbank and Deysher (1927) has already been mentioned in this regard. In connection with the use of inert gases to fill the

TABLE XXXIII. Absorption of gases by edible oils and fats at 23 to 26°C.
(F. C. Vibrans 1935)

	Gas per 100 cc. of oil (cc.)		
	Nitrogen	Hydrogen	Carbon dioxide
Corn oil..............................	6.3	4.1	.....
Cottonseed oil........................	6.1	4.2	134.0
Bleached lard........................	6.2	4.3	102.0
Hydrogenated cottonseed oil............	6.7	4.3	.....

head space above stored oils, the solubilities of such gases in the oils are of some importance. The data given in table XXXIII are taken from the work of Vibrans (1935), and show the solubilities of nitrogen, hydrogen and carbon dioxide in various vegetable oils. The very great solubility of carbon dioxide is to be noted. This behaviour of carbon dioxide has also been reported by Schmidt-Nielsen (1927), who found that at 20°C. various animal and vegetable oils dissolved between 117 and 160 cc. of the gas per 100 g. of oil. Experiments made by the writers show that pilchard oil and cod liver oil absorb 150 cc. and 120 cc. per 100 g. of oil at 23°C. respectively.

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SECTION 7. PRODUCTION OF FISH OILS

The production of oils or fats from animal raw materials consists essentially of three processes: (1) rendering or liberation of the oil from the tissue cells, (2) separation of the oil from the tissue material, and (3) separation of the oil from the accompanying "stick-water." In the case of fish oils the methods and machinery used for the first two of these processes depend largely upon the type of raw material being processed. The method of separation of oil from the accompanying "stick-water" is not entirely dependent upon the nature of the raw material, as any suitable separatory method can be used once the oil has been removed from the tissue. The first two processes will therefore be discussed according to the nature of the raw material, whilst the last process will be considered separately.

I. PRODUCTION OF FISH OILS ACCORDING TO RAW MATERIAL

(a) FISH LIVERS OF HIGH OIL CONTENT

Under this heading are included such materials as cod, haddock, hake, shark and dogfish livers, the oil content of which may vary from 30 to 80 per cent. The oil from this class of liver is relatively easy to extract. It is present in large amounts and is not easily re-absorbed by the coagulated protein of the liver.

(i) "SUN-ROTTING" PROCESS

In this method the livers were hung in bags and the oil collected as it dripped from the rotting tissue, or the livers were placed in barrels and the oil skimmed from the surface as rotting took place. The oils so produced were high in free fatty acids and had a dark colour and foul odour. The process has largely been superseded by modern methods.

(ii) DIRECT STEAM METHODS

The treatment of livers with direct steam is the most popular of the modern methods. The type of plant used depends largely upon whether the livers are to be rendered at sea or on shore. In Norway and Newfoundland cod-fishing is a "shore" fishery and the livers can be landed in good condition. Codfish landed in Great Britain and in the Maritime provinces of Canada are usually brought in by trawlers which may remain at sea for some days before landing their catch. Such trawlers are fitted up with small liver boilers of the type illustrated in figure 31. These are so designed that they may be operated both in calm and in stormy weather. They consist essentially of a vertical boiler with a conical top on which is a tall stack. A port on the top of the cooker allows for the introduction of the livers. This port is then closed and steam allowed to enter the cooker by means

of a perforated coiled pipe on the bottom of the boiler. The livers are heated for a certain time, after which water is forced into the boiler. The oil is thus forced up the stack and out through a side pipe. It is then filtered and run to storage tanks. The temperature at which the steam enters these cookers varies greatly with individual installations, but is usually about 293°F. (60 lb. per sq. in.). The use of these cookers at sea allows the production of a first class medicinal cod liver oil from absolutely fresh livers. As with any simple steam rendering plant of this kind, some of the oil fails to be removed from the coagulated liver material, but, further rendering of the livers being impractical at sea, the gurry is usually dumped, and the boilers flushed out with water, when they are ready for another
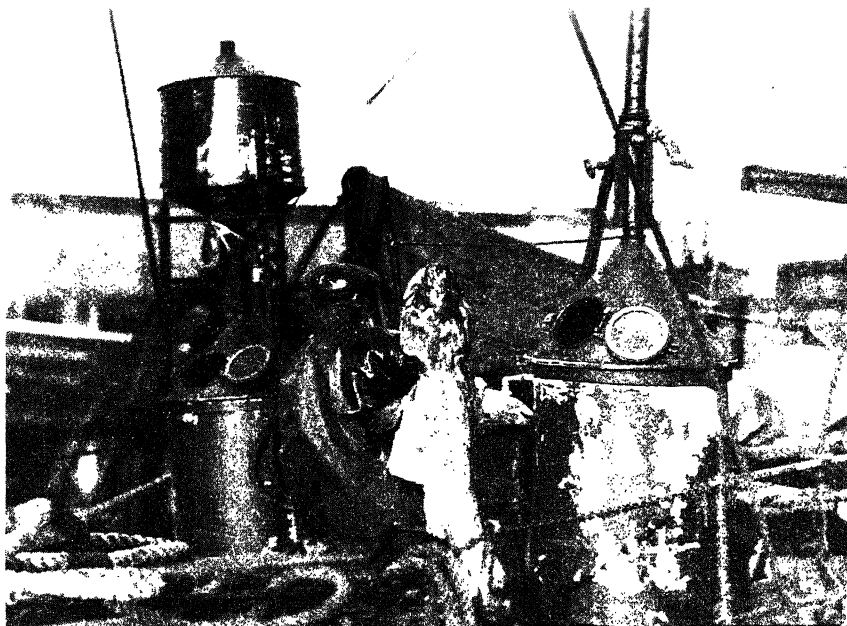
FIGURE 31. Cod liver oil extractor aboard a trawler (Courtesy of Maritime National Fish Ltd., Halifax).

charge of livers. The oil yield by this method runs about one-half the weight of the livers.

At many places along the Atlantic coast of Canada the rendering of cod livers on shore is carried out by individual fishermen, who in the past have used the sun-rendering method or various simple methods wherein the livers were boiled with water and the oil skimmed off. Recently, Dr. A. Labrie (1937) of the Gaspé Fisheries Experimental Station, Fisheries Research Board of Canada, designed a novel apparatus which allows the production of a first grade medicinal cod liver oil on a relatively small scale. The principle of this apparatus, a plan of which is shown in figure 32, is that of a percolator in which the extracting agent is steam, replacing boiling

FIGURE 32. Small-scale extractor of cod liver oil (Labrie).

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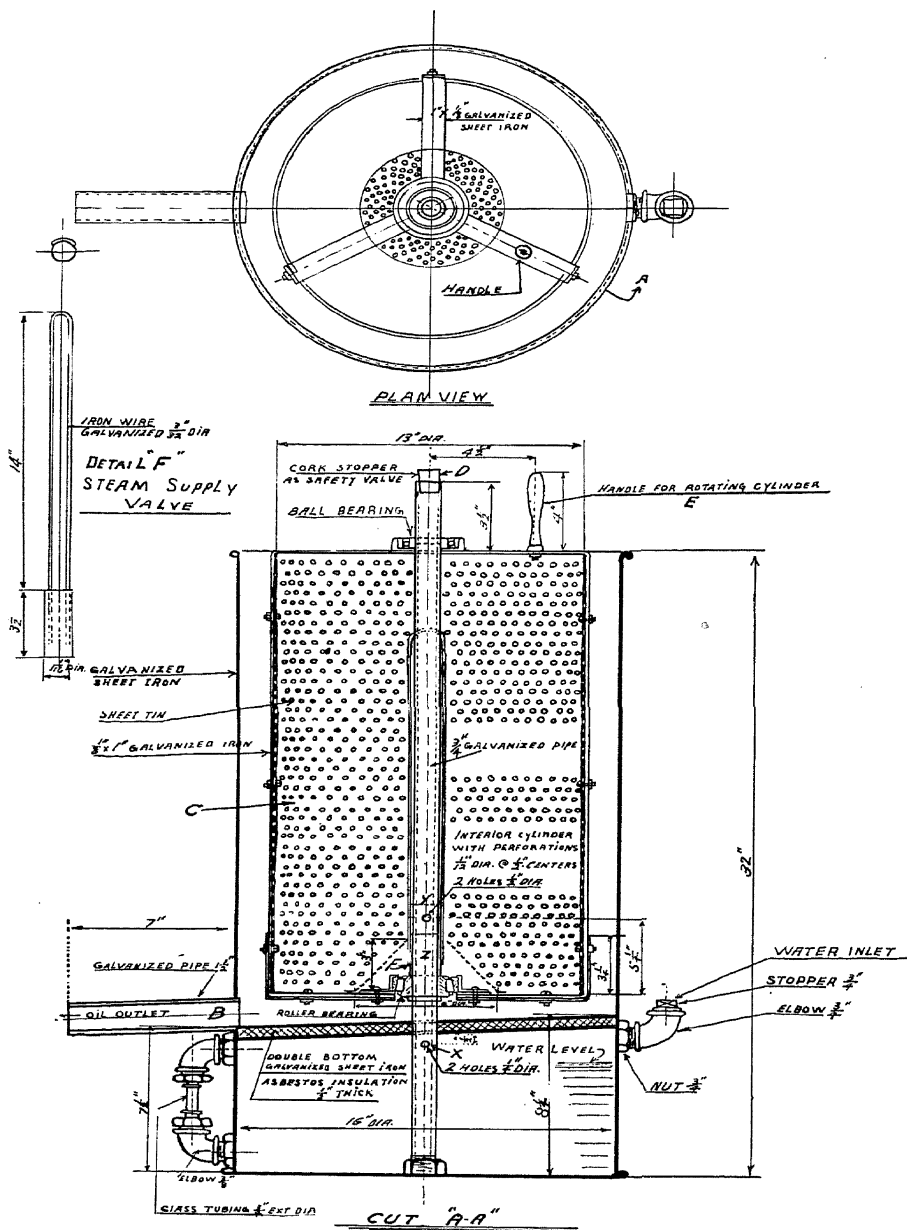
water.   The whole is constructed from galvanized sheet iron, and can be placed on an ordinary stove or over a convenient fire.   The lower reservoir is filled with three quarts of water.   On boiling, the water is converted into steam which moves through the pipe Z, entering Z through the holes X and entering the upper reservoir through the holes Y.   In proportion to the extraction, the oil flows through the perforations at C, down the annular space and out through the opening at B.   The outer cylinder is insulated with a layer of asbestos.   The cylinder in which the livers are placed is made of galvanized sheet iron, and is pierced with holes one-twelfth inch in diameter spaced every half-inch.   This cylinder is supported in the apparatus by the steam pipe running on ball bearings.   The steam pipe is then fixed solidly to the two ends of the apparatus.   In this manner, the cylinder which contains the livers can be conveniently turned around the steam pipe as axis.   A simple arrangement permits shutting of the holes Y during filling of the cylinder with livers, and consists of a sleeve which fits over the steam pipe.   This is simply lowered by means of an iron wire handle till it shuts off the holes Y.   The rubber or cork stopper at the top of the steam pipe acts as a safety valve.

The water in the lower reservoir is brought to a boil.   The livers are then placed in the cylinder, the sleeve is raised and the top of the steam pipe closed with the stopper D.   Boiling is continued for about 5 hours during which time fresh lots of livers are added.   It is necessary to agitate the livers from time to time with a stick to ensure that all the livers come in contact with the steam.   Towards the end of the operation, the cylinder can be easily turned by the handle E. Boiling is continued as long as oil flows from the digester.   It is possible to obtain 80 per cent of the oil contained in cod and similar livers with this apparatus without having to press the residue.

The oil flows through a cloth-bag filter into a separator, which consists simply of a galvanized iron box fitted with two outlets, one at the bottom and one half-way up the side.   After separation, the oil is run off through the side outlet, a suitable oil level being maintained by adjustment of the water level in the tank through the bottom outlet.

The chief advantage of this extractor is the ability to produce good commercial oil without the necessity of a steam boiler.   An apparatus with external dimensions (inches) $32'' \times 16''$, having a cylinder $24'' \times 13''$, should have an extraction capacity of 15 gallons of livers every 5 hours. One with over-all dimensions $36'' \times 18''$ with a cylinder $28'' \times 15''$ should have a capacity of 25 gallons of livers every six hours.   The apparatus is easy to construct and should not cost more than 25 dollars.

In commercial shore establishments the livers are usually placed in large conical tanks, down the centre of which runs a perforated steam pipe.   Steam at a pressure of 60 to 80 lb. is admitted and the whole mass brought to a gentle boil. After the livers have been disintegrated, the oil is withdrawn either by means of a swivel-pipe or by flowing the oil up to an overflow pipe by means of water.   The oil is immediately filtered to remove small pieces of liver debris, and is then tanked ready for the chilling process.   In the more modern plants the oil coming from the digesters is put through centrifuges which take out the debris and water. The clear oil is then cooled to about 35°F. and the stearine removed by filtration. The clear filtrate is the non-freezing medicinal cod liver oil of commerce.   A simple shore extraction plant is shown in figure 33.

In connection with the production of medicinal cod liver oil, the Norwegian Government has outlined certain regulations that must be followed.   The most important of these, according to Arentz and Lund (in Hefter-Schönfeld 1936, p. 852), are as follows: In the preparation of medicinal oil, only cod, coalfish and haddock livers may be used.   These livers must not be bruised in any way but must be properly packed in suitable casks.   The casks must be thoroughly cleaned

out each day. The livers must have no gall bladders adhering to them. Putrefied livers are not permitted in the production of medicinal liver oil. In the production of the oil by steam-jacketed kettles, the livers must be heated to 70 to 75°C. (158 to 167°F.) with constant stirring, in order to disintegrate the livers. When the livers are treated in open kettles with direct steam, the temperature may be raised to 85 to 90°C. (185 to 192°F.). After steaming, the mixture must be allowed to remain quiet for one hour before passing the oil over into the cold-clearing tanks. The filtration, cooling, and other tanks must be filled as completely as possible and kept well covered to eliminate the influence of air and
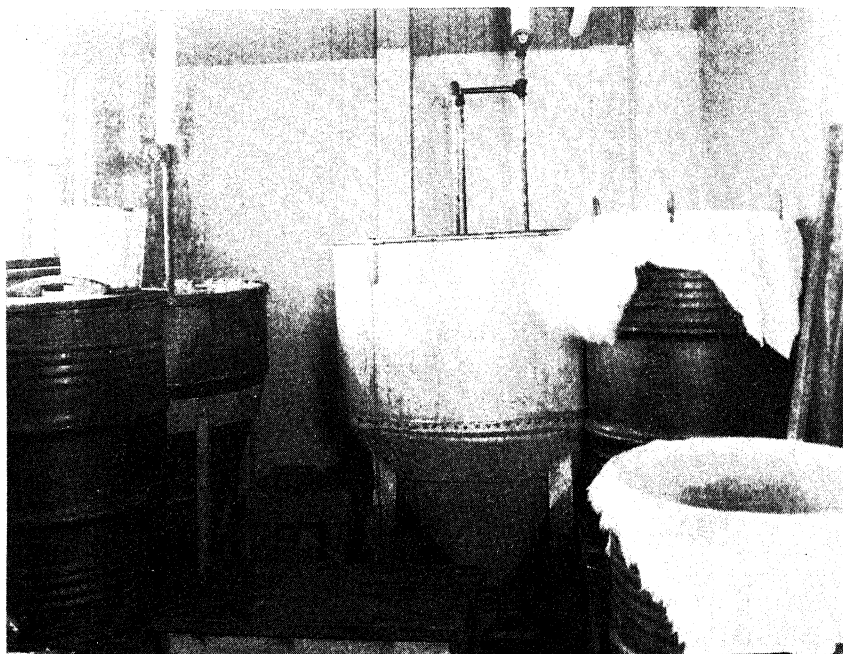
FIGURE 33. Simple shore extraction plant for cod livers (Courtesy Lunenburg Sea Products Co.).

light. From the filled barrels the sediment must be removed every week or so, as this sediment injures the odour of the oil. Oil which is extracted from the liver residue either by pressing or by other means, must be declared a second grade oil.

Specific and stringent regulations also apply to the medicinal cod liver oil trade in Newfoundland. Only cod livers are permitted for the manufacture of the medicinal grade of cod liver oil and these must be fresh, and not exposed to the air for more than two hours before boiling. Gall bladders must be removed, and the livers sorted and washed with fresh water. The boiling pan must be kept scrupulously clean. The livers are boiled with live steam (75 to 80 lb. pressure) until a white scum floats. This means about thirty minutes' actual boiling.

During boiling, constant stirring of the livers is recommended. After turning off the steam, the contents of the boiling pan are allowed to settle *not more than five minutes* when the top oil is skimmed or dipped off, and goes direct to the cooling tank. The cooling tank is made of galvanized iron with a floating cover to protect the oil from contact with the air. The oil enters the tank through a funnel covered with straining cloths to catch any pieces of debris. The oil remains in the cooling tank for thirty-six hours until it is cold enough to strain. It is then filtered through double calico bags directly into tin-lined barrels. Such barrels must be kept in a cool place and protected from the sunlight.

The residue in the boiling tanks is then treated with cold water and steamed again. The excess water is removed from the bottom of the tank, and the hot liver mixture pressed in bags in a hand or hydraulic press. This oil is suitable for poultry feeding purposes. The liver pressings are placed in stout wooden barrels whilst still hot in order to keep them sterile.

Drummond and Hilditch (1930) made a very comprehensive study of the cod liver oil industry and their report should be carefully read by those interested in the production of medicinal fish liver oils. In regard to the production of cod liver oil, these authors recommend the use of steam at a pressure of 80 to 100 lb. per square inch. They claim that the vitamin content of the oil does not appear to suffer in any way when high-pressure steam is employed, whilst the yield of oil, and its separation from the "foots" are better under these conditions. Owing to the transitory high temperatures attained by the use of such high pressure steam, the liberation of the oil from the livers is completed more rapidly, and, what is more important, the treatment ensures the complete inactivation of the enzymes present in the liver material. These authors find that steam at pressures of 30 to 60 lb. per square inch is also quite efficient, provided that the steaming time is extended.

Experiments carried out in these laboratories (Swain, unpub.) on gray cod livers, showed that the chief effect of temperature of digestion was on the oil yield. Livers digested at 50°C. gave a yield of 1.9 per cent, whilst treatment with open steam at 100°C. gave 8.2 per cent. The vitamin A potency of the oils was identical. In both cases, allowing the coagulated livers to stand overnight before removing the oil increased the yield, but then the livers treated at 50°C. gave an oil slightly higher in free fatty acids than those treated at 100°C.

(iii) INDIRECT STEAM OR SO-CALLED "VACUUM" METHODS

In the belief that loss of vitamin A occurs in the livers during the ordinary steaming methods, many plants have been designed to operate under reduced pressures and at comparatively low temperatures. It is claimed that a higher yield of oil is obtained by such methods, but whether the extra cost is warranted is a matter for individual operators to decide. These plants are made in both vertical and horizontal styles. Typical of the former is the Scott Patent Vacuum Boiler shown in figure 34. This is a jacketed boiler fitted with stirring paddles and designed to operate under reduced pressure, low pressure steam or hot water being used for heating purposes. The livers are fed into the machine through a controlled feed valve. Owing to the combination of low pressure (which hastens

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the rupture of the cells) and mechanical agitation, rendering of the livers takes place rapidly. The behaviour of the material during processing can be followed by suitably arranged sight glasses. The apparatus is equipped with a decanting pipe by means of which the supernatant oil can be removed. The liver foots are
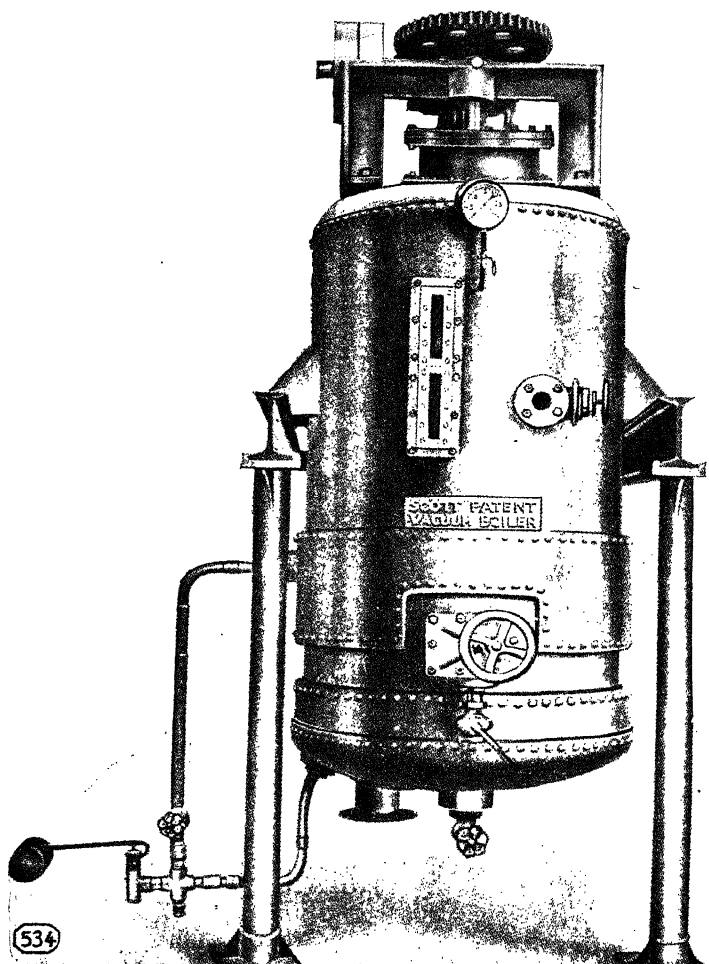
FIGURE 34. Scott's vacuum boiler.

removed through a drain in the bottom and pass to a solvent plant where the last trace of oil is recovered.

The horizontal type of low pressure extractor is illustrated by the design of O. Wilhelm, a diagram of which is given in figure 35. The complete equipment consists of an extractor 1 which is made of aluminium, the receiving tank 2, vacuum pump 3, the hot-water container 4, and the

steam pump 5. Warm water at 60°C. is pumped through the outer jacket of the aluminium extractor 1 and recirculated through the heater by means of the steam pump. The extractor is equipped with a perforated false floor. In operation the extractor is first heated and the livers charged through the upper manhole. The extractor is then rotated during the digestion period, the circulating water being maintained at 60°C. After digestion is complete, the outlet valve on the extractor is connected to the oil receiver and vacuum pump by means of a flexible metal pipe. The free oil is pumped over, after which the extractor is rotated again for a further period. It is claimed that a high yield of first grade medicinal oil is obtained with this system.

There are many other designs of equipment for the low-pressure extraction of cod and similar liver oils. They all consist essentially of jacketed extractors equipped with mechanical agitators and may, or may not, digest under reduced pressure. The temperature range over which these types of extractors are designed to work appears to be from 60° to 80°C. (140 to 176°F.).
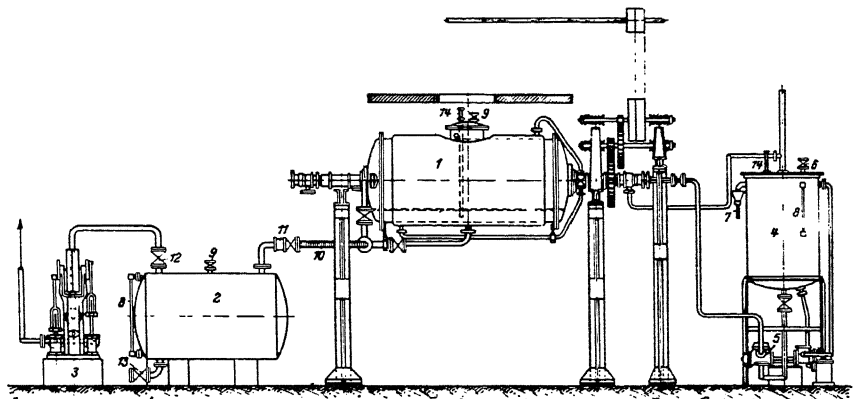
FIGURE 35. Wilhelm low-pressure liver oil extractor.

(iv) EXTRACTION WITHOUT HEAT

In U.S. patent 1,519,779 there is described a method for the production of non-freezing medicinal cod liver oil from cod livers without the use of heat. According to the patent this is accomplished by subjecting the fresh livers to a temperature several degrees below the freezing point, and maintaining them in a frozen condition until the oil is pressed from them. The apparatus described to accomplish this is a jacketed glass-lined tank in which the livers are placed. A freezing mixture is circulated through the jacket to freeze the contents. The frozen mass is then pressed to extract the oil, the livers being kept frozen during the process. It is claimed that this procedure yields a larger quantity of first grade oil, having less odour and colour, than that made by the steaming process.

This particular form of manufacture of cod liver oil has been examined by Stewart (1930) at the Atlantic Fisheries Experimental Station of the Fisheries Research Board of Canada. Stewart found that by freezing and pressing, more oil could be obtained from a given sample of livers, than was possible by skimming

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it off in the usual cooking process. However, the foots from the pressed frozen livers still contained a quantity of oil that could possibly be recovered as a second grade material. It is claimed that the vitamin A content of the oil made by this process was the same as that made by the steaming method.

U.S. patent 2,134,163 describes a method by Wentworth in which oil is expressed from fish livers such as cod without the use of heat. In this method, the livers, after washing with a saline solution, are mechanically disintegrated and mixed with a smaller proportion of dry beet pulp or dehydrated cereal grain pulp. Dehydration of the liver cells takes place and, presumably, coagulation of the liver proteins, with the resultant liberation of the oil. The first oil that separates is run off, and the remainder is recovered by cold pressing. Samples of cod liver oil made by this process from portions of a thoroughly mixed lot of livers, and by the steaming process, were examined in these laboratories and found to be identical in vitamin A potency. After standing in a refrigerator for one year in filled bottles, the acid values of these oils were both below one.

It should be emphasized once again, however, that the fat-splitting enzymes found in fish are extraordinarily active, and in any low temperature method of liver oil extraction these enzymes may not be entirely destroyed. As long as the oil so produced has a moisture content lower than 0.3 per cent, such enzymes would not function, but, as pointed out by Drummond and Hilditch (1930), it is a wise precaution to heat such oils promptly after extraction in order to sterilize them.

(v) MISCELLANEOUS METHODS

Various other methods have been suggested or patented for the production of oil from fish livers such as cod and the like. U.S. patent 1,833,061 claims that by lowering the pH of the ground livers to about 1.5 the "fish oil contained in the liver is separated out as an independent phase. By a supplementary centrifugation 99 per cent of the fish oil contained in the liver may be recovered." The writer has tried this method with various kinds of fish livers. With oily livers such as dogfish, some oil is obtained, but the beneficial effect of the high acidity is doubtful. Furthermore, the yields are never as good as those obtained by the simplest steaming and skimming process. Another process which has been used with some success, particularly with various shark livers, is to steam the livers in suitable kettles in the usual manner, but with the addition of about 1 per cent caustic soda. This puts the liver proteins sufficiently into solution to allow the use of high-speed non-sludging centrifuges, a procedure that otherwise could not be used on account of the plugging of the machine with the coagulated liver material.

Clear sparkling oils of low free-fatty-acid content are usually obtained by this method. The chief disadvantage is that an alkali-refined oil is obtained with a consequent low stability against oxidative rancidity. In addition, great care has to be taken to prevent loss of vitamins by adsorption by the dissolved soaps. Both of these subjects are treated elsewhere in this Bulletin.

(b) Fish Livers of Low Oil Content

Such materials as halibut, salmon, black cod, tuna and similar fish livers are included under this heading. All these livers have two common characteristics: they have a low oil content (from 5 to 30 per cent) and the heat coagulated proteins have a strong tendency to reabsorb the liberated oil. Steaming methods such as are used for cod livers are of no value in this case, and more elaborate methods have to be used. Several years ago solvent extraction methods were employed, but these were quickly superseded by methods which had for their object the digestion of the liver proteins into a soluble form, from which the oil could be extracted. Although most of the methods used by commercial firms are kept "secret", there are a few patents dealing with this subject. Whether or not they are all valid does not concern us in this discussion.

(i) solvent extraction

U.S. patent 2,078,404 describes a method in which the fish livers are steamed at a temperature not substantially higher than 100°C. (212°F.), and the liberated watery phase thus produced filtered off. The pasty liver material is then frozen and the oil extracted with a solvent, such as ethyl ether. The latter should be peroxide-free. The solvent is subsequently removed from the oil by distillation under reduced pressure. The livers are protected from the air during the whole process. The writer has examined this process in connection with the extraction of oil from halibut livers. An excellent yield of good quality oil was obtained. The oil was, however, slightly darker in colour than that obtained by methods to be described below and, of course, contained all the free fatty acids that were present in the oil in the original livers.

Another extraction method is described in U.S. patent 2,067,279 as follows: "The oil is obtained by extracting the liver (the protein of which has been coagulated by processes or agents non-injurious to vitamins A and D, as by cooking or by adding alkali) with a solvent, preferably one selected from the group consisting of ethylene dichloride, trichlorethylene and dichlorethyl ether. The extraction is made, preferably after adjusting the weight ratio of water to "dry" (which is used to mean water-free and oil-free) liver in the extraction mass to between 2 and 4 of the former to 1 of the latter, the adjustment being effected by adding water to the extraction mass to supply a deficiency, or by evaporating with heat and/or under reduced pressure, to remove an excess." By thus maximizing the completeness and speed with which the solvent separates from the liver tissue, this method, it is claimed, enables one to obtain quickly practically all the oil contained in the liver. The writer has had no experience with this method.

(ii) digestion methods

Of the patents describing digestion of the liver material, the following three will suffice to show the trend in these processes. British patent 293,277 outlines a combination freezing and alkali-digestion method. The raw material is first frozen, to effect a partial liberation of the oil during rupture of the cells by the ice crystals formed. Whilst in the frozen condition, the material is passed through a mincing machine in order to break up the tissue thoroughly. The frozen pulp is allowed to thaw at normal temperature and is then treated with two to three times its volume of 1.5 per cent caustic soda solution, and the whole mass raised

to 40°C. (104°F.), preferably by means of live steam. The material is thoroughly mixed during 15 minutes and allowed to stand at the same temperature for five or six hours. The liberated oil or fat is then separated by suitable methods.

A digestion process using the vegetable enzyme(s) papain (obtained from the fruit of the papaya tree) is described in U.S. patent 1,922,484. In applying this method to fish livers, the material is minced and brought to a temperature of 70 to 80°C. (158 to 176°F.) and to a pH of 4.5 to 5.0. One-half per cent of papain in aqueous suspension is then added and digestion allowed to proceed until lique-faction occurs. (It is claimed that from 10 to 30 minutes is sufficient.) The tem-perature is kept well above the melting point of the fat or oil to be extracted, and the material is centrifuged or allowed to settle by gravity. It is claimed that the separation can be made either at an acid or alkaline pH, but not at the iso-electric point of the protein. On applying this method to halibut and salmon livers, the writer and his associates were not able to obtain satisfactory results, particularly with regard to speed and completeness of digestion. Lower yields of oil were obtained with this method than with others.

According to British patent 465,547 (issued May 10, 1937) the inventor adds a dilute aqueous alkali solution to the liver material and heats to dissolve the protein. A fatty oil is then added to the mixture to dissolve out the original liver oil and its vitamins. A method similar to this was described by Brocklesby and Green in 1934. Another British patent, 486,277, describes the boiling of cod, halibut and other fish livers with solid alkali hydroxide. The mixture is allowed to cool and settle. The separation of oil and water may be effected by adding a solution of aluminium sulphate or other acid liquid to break the emulsion, and passing the whole through a centrifuge. In the writer's experience this procedure is not easily carried out. It is usually impossible to separate the digested pro-tein material completely from the oil and water emulsion. If an acid reagent is added, the protein is reprecipitated and the oil reabsorbed. It is usually necessary to centrifuge the whole mixture first, and then, if the oil comes out as an emulsion, to break it by a careful adjustment of the pH with an acid solution.

Brocklesby and Green (1934, 1937) described experiments with three methods for the production of oils from fish livers of low oil content. The first of these consisted of coagulating the liver proteins in various ways, in order to produce a coagulum that would withstand high pressures in a hydraulic press. By the addition of various coagulating salts, and also by the use of pressure cooking, the livers (halibut) were fibrous enough to withstand pressing at 9,000 to 10,000 pounds per square inch before they squeezed through the press cloth. Livers steamed in the ordinary way will be forced through the cloth at pressures below 1,000 pounds. Even at 10,000 pounds pressure only 50 per cent of the oil was recovered and it was not of satisfactory quality.

Earlier experiments, in which the livers were steam-coagulated in the presence of various electrolytes, and the diluted mixture put through a 3-phase centrifuge, showed that the solid-to-oil ratio was so high that little oil could be separated before the accumulated solids, saturated with oil, had to be dumped. Efforts were therefore made to reduce this solid-to-oil ratio. Certain livers, namely those that had undergone considerable hydrolysis, were dissolved satisfactorily

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by heating gently with a dilute solution of sodium carbonate. Fresh livers, however, had to be heated with caustic soda with the attendant difficulties due to soap formation. Enzyme digestion was therefore tried, and after considerable experimental work the following process was evolved. The livers are minced and diluted with an equal quantity of water, and sufficient dilute hydrochloric acid added to reduce the pH value to between 1.2 and 1.5. The pH is maintained within this range during the digestion period. Commercial pepsin, to the amount of 0.05 to 0.1 per cent of the fresh livers, is then added dissolved in a little warm water. The mixture is well stirred and maintained at a temperature of 110 to 120°F. for a period of between 24 and 48 hours, during which time it is slowly stirred and protected from the air. The end of the digestion period is ascertained by testing small samples with a solution of sodium carbonate. When a sufficiently clear solution is obtained, the main batch of material is heated up to 175°F. and treated with a saturated solution of sodium carbonate, and then passed through a centrifuge. With fresh livers a yield of 90 to 95 per cent of the oil is obtained. This oil is lemon yellow in colour and, of course, practically without free fatty acids. The low pH maintained during the digestion process prevents bacterial action and, since the optimum pH for fat-splitting enzymes is above pH 5, the action of any of these enzymes present in the liver is inhibited. The concentration of the hydrochloric acid used in the digestion process is so low that there is no chemical hydrolysis of the oil during the process, and consequently, if the oil in the livers is low in free fatty acids to begin with, that is, if the livers are fresh and in good condition, no troublesome emulsions are encountered when the sodium carbonate solution is added. Halibut livers are not always landed fresh, however, and the free fatty acids are converted into sodium soaps which are lost in the wash-water from the centrifuge. This loss would be immaterial were it not for the fact that this soap solution carries with it considerable vitamin A [see Section 8 I (a) for an account of the work on adsorption of vitamin A by soaps]. This can be recovered by adding to the alkaline wash waters a quantity of edible fish or vegetable oil, stirring thoroughly, and passing through a centrifuge. This oil acts as a solvent and removes the vitamin A from the soap solution. Where highly potent oils have been processed it may be necessary to repeat this step several times. By using a countercurrent principle, wherein the first extraction of the wash waters is carried out with an oil already fortified with vitamin A from a previous extraction, and the second, third, etc., extractions are made with oils of progressively lower vitamin A potency, practically all of the vitamin A remaining in the original wash liquors can be recovered.

This oil-solvent process had already been tried by the above-mentioned authors directly on sterilized livers with very good results. In some livers, e.g. salmon livers, the oil content is so low that even by the pepsin digestion method little, if any, oil is obtained. The only feasible way to remove oil when it is present in such a small amount is by some solvent process such as dissolving out the liver oil, and the attendant vitamins, by another oil. There are various methods of treating the liver material in this process. They may be simply steamed, finely disintegrated and dispersed in the solvent oil. More efficient methods, however, consist in digesting the liver material either by alkali or by enzymes, followed by intimate mixing with the solvent oil. In all cases the liver material and water are removed from the oil by centrifugal methods.

The apparatus used for these methods is very simple. If pepsin digestion of the livers is to be used, the digestion tanks should be of some acid-resisting material of which there are many now available on the market. The tank should be jacketed and some means provided for circulating water at constant temperature. Suitable covers and stirring equipment should be included in the equipment. For alkali digestion a jacketed iron tank is suitable. All tanks should be equipped with an open steam coil and suitable outlets. The type of centrifuge

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to be used will depend largely upon the size of the plant and the other uses to which the centrifuge is to be put. The writer has seen both purifier and sludging types of centrifuges operate satisfactorily on digested liver material.

(c) Fish Intestines

The recent discovery that oils rich in vitamin A can be obtained from the intestines of such fish as halibut, black cod, etc., has led to the commercializing of this material as a source of vitamins and, of course, a search for a suitable method of extraction. This material is harder to process than the livers, and with both alkali and enzymatic digestion methods, considerable amounts of tissue remain undigested. Furthermore, this material undergoes much more rapid decomposition, both autolytic and bacterial, than is the case with livers. Consequently, the free-fatty-acid content of the oil in the intestines when they reach the processing plant is usually very high, and emulsification troubles follow when the material is alkali-treated. The low oil content of the intestines is also a disturbing factor. A further complication seems to be that the alkali-peptized proteins of intestines have a greater adsorption capacity than those of liver, and greater amounts of oil and vitamin are held by them than is the case with the peptized liver proteins. So far as the writer is aware, no satisfactory method has yet been found for the treatment of fish intestines. Those plants that are operating on this material use either enzymatic or alkali digestion methods, but in all cases certain modifications are made in the procedure. The nature of these modifications is, of course, kept secret.

From the writer's experience with the extraction of these intestines, the suggestion might be made that methods other than digestion should be sought. One promising lead, which up to the present has not yet been fully investigated, seems to be in sterilizing and coagulating as far as possible with steam, filtering and pressing out as much excess water as possible, and then solvent extracting. Unfortunately, the water content of the sterilized material is too high to permit direct extraction, and drying entails too great an expense and loss of vitamins. Mechanical elimination of the water from intestinal raw material is a requisite preliminary step. When this can be accomplished economically, the treatment of the partly dehydrated viscera will be much simplified.

(d) Whole Fish and Fish Offal

The production of fish oils from herring, sardines, pilchards and the offal of salmon canneries, herring packers, etc., is carried out by various modifications of either the pressure process or the solvent extraction process. It should be noted at once that, where large quantities of material are to be handled, the pressure extractors are almost universally used. This applies to the production of oil from herring, pilchards, sardines and salmon cannery offal on the Pacific coast of North America, menhaden and herring on the Atlantic coast, and herring in Iceland and Norway. In places where oily fish material is available only in small quantities, the solvent process is used. The capacity of solvent plants is, in general, much

smaller than that of pressure extraction plants. Two complicating factors enter into any discussion of the relative merits of solvent versus pressure extraction. The first of these is that the production of fish meal at the present time is of more economic importance than that of the fish oil, and the design of a plant must of necessity be considered in the light of fish meal production. In the second place, fish oil obtained from most, if not actually all types of solvent extractors, is of poorer quality than that made by pressure extractors. Solvent oils are usually of a darker colour than pressed oils. On the other hand, it must be admitted that the amount of meal and oil recovered in a solvent plant is higher than that in a press-equipped plant, and furthermore the meal is usually of better quality, having an oil content not higher than 2 per cent. Such meal can therefore compete with those of the "whitefish" grade. Per unit capacity, solvent plants are reputed to be more expensive to install and operate than the simpler pressure-type plants. It is obvious, therefore, that in choosing the most desirable type of plant, the economics involved are quite complicated.

In the following discussion of equipment no attempt will be made to consider relative costs. The points of interest are efficiency of production, yields and quality of the oil.

(i) BATCH-TYPE PRESSURE EXTRACTORS

Discontinuous or batch systems for the production of fish meal and oil are not in general use in either the United States or Canada, but a few plants of this kind are still in operation. In Europe they are more common, particularly where the less oily fish are being processed. The equipment of such plants usually consists of cookers, presses, driers for the meal and settling and storage tanks for the oil. Usually some provision is made for the transportation of material to and from each piece of equipment, but the cookers and presses only handle one charge at a time. This type of plant has certain advantages over the continuous system, advantages that are, however, being rapidly eliminated as the design of the latter type of plant continues to be improved. In factories where a variety of raw material has to be handled, the batch system permits of greater flexibility in regard to time and conditions of cooking, pressure and rate of pressing, etc. Each batch of raw material can be put through the plant under the most suitable conditions.

There are many designs available for batch cookers. Some of these are jacketed and many can be operated under either pressure or partial vacuum. The kinds most generally used today are jacketed and operate under a partial vacuum. The time of cooking depends upon the material and upon the type of pressing. If wet pressing is to be used, the cooking time is relatively short, the object being merely to break the oil cells and to sterilize the material. If dry pressing is to be used, a higher vacuum is preferred and the water is removed during a cooking time that may extend to 6 or 7 hours. Steam pressures in the jacket of the cooker vary between 40 and 80 pounds per square inch.

Hydraulic presses are usually used in batch systems. They may be used with curbs or by building up layers of the cooked material in folds of canvas.

The rate of pressing can be closely controlled by the speed of the pump, and many materials that give trouble in continuous presses can be satisfactorily handled in the hydraulic press. Their main disadvantages are low capacity and high labour requirements. Martin (1939) has also criticized the use of hydraulic presses for the extraction of oil and water from cooked fish material on the grounds that they give deficient extraction of oil and imperfect dehydration. These criticisms are true to a certain extent, but for reasons given later in this discussion, they also apply to other mechanical means of removing oil and water from cooked fish material.

If the cooked fish are pressed wet, the oil and water mixture, very often partly emulsified by reason of the dissolved nitrogenous material in the water, is pumped to a settling tank system. The expressate from dry pressed fish usually
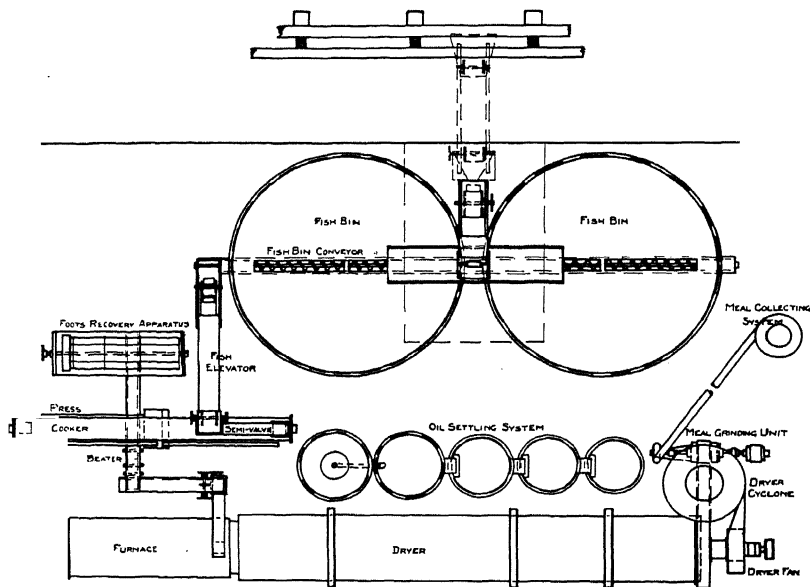
FIGURE 36. Plan for continuous reduction plant (Courtesy California Press Mfg. Co.).

contains some finely-divided protein material and a little water. This mixture is usually allowed to stand in a heated tank until the debris has settled, when the clear oil is pumped to storage. Oil produced by the dry rendering method is nearly always of a dark colour, irrespective of the nature or degree of freshness of the raw material.

(ii) CONTINUOUS-SYSTEM PRESSURE EXTRACTORS

This type of plant is in general use where such fish as herring, sardines and pilchard are being processed. The system consists essentially of continuous cookers, presses, driers and oil separating equipment. A plan and illustration of a modern plant are shown in figures 36 and 37. The cookers are long stationary

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cylinders through which the fish are passed continuously by means of a revolving screw arrangement. Live steam is fed into the cylinder by means of a series of small inlet pipes placed at equal intervals along the bottom of the cooker. Suitable arrangements on the inlet and outlet ports prevent the escape of steam. Choking the cooker with fish enables the operator to cook under pressure. The pressure of the steam during cooking depends upon the nature of the fish being processed, but is usually about 10 pounds per square inch at the feed end, and 5 pounds at the discharge end. The cooking process has to be carried out correctly, as upon the success of this operation will depend the pressing properties of the cooked material. Most operators gauge the success of the cook by removing a whole fish from the sampling door at the end of the cooker. If the fish has received the proper amount of cooking, a slight shake by the tail should free the meat from the backbone readily, and no free blood should show. The meat should be firm, white, and only slightly shrunken from the vertebrae.

From the cooker the material passes through the outlet valve immediately into the feed box of the continuous screw press. A modern design of such a press is shown in figure 38. The press consists essentially of two screws of different pitches working within a curb. The feed screw is built on a shaft of uniform diameter, and has a slightly higher pitch than the pressure screw which is built on a tapering shaft. The diameter of this shaft increases towards the discharge end of the machine. The discharge takes place through the annular opening at the end of the pressure screw, the size of this opening being regulated by the pressure cone. In some models, a rotating knife engages with the feed worm and prevents the material from turning with the screw. Nearly all models are equipped with some means of injecting steam or water into the press. The curb is built in two ways. In the earlier designs, the curbs consisted of steel slats arranged radially around the worm, and held in position by metal bands. These steel slats were slightly wider on the inner side and, since they were arranged lengthwise, thus forming the circumference of the curb, the distance between them was greater on the outside than on the inside. This arrangement minimized the possibility of the curb becoming plugged with small pieces of fish flesh forced through the openings. Modern curbs consist of perforated brass cylinders strengthened by a metal framework that permits the use of very high pressures. The holes in this cylinder are tapered, the smaller opening being on the inside, thus preventing blocking. In operation, two plugs of fish are formed, one at the discharge pressure-cone and one in the compression chamber between the two screws, and between these two plugs the material is gradually subjected to an increasing pressure. There is a certain amount of churning action in these presses, with the consequent change in the surface of the material being pressed in relation to the curb. This allows more uniform removal of the water and oil, since in a stationary press cake it is well known that the moisture and oil content vary with the distance from the centre of the cake.

The liquid that flows from the continuous press consists of a mixture of oil and "stick-water". The latter usually has considerable quantities of dissolved

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FIGURE 37.   Modern fish reduction plant.   (A) cooker and oil recovery syste
(B) adjusting steam pressure on cooker.

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(C) continuous presses; (D) fish meal dryer.   (Courtesy B.C. Packers Ltd.).

nitrogenous material in it. In addition, the mixture usually contains a certain amount of finely divided protein material which promotes the formation of emulsions. This mixture is first passed to a "foots-recovery" system, which consists of a long rotating cylinder of fine mesh screen (usually 40 meshes to the inch) and a small, especially designed continuous press. The liquid mixture is fed into the inside of the rotating screen, which removes a quantity of the finely divided protein. This is pressed in the small press, and the effluent from this press, plus the liquors filtering through the screen, are then pumped to the oil recovery system. In the case of the press liquor from herring it is the common practice in British Columbia to lead the liquor by gravity from the presses to settling tanks where the oil is allowed to break. The aqueous liquor is then passed through the foots-recovery system.

Efforts are continually being made to improve the design of presses so that the maximum amount of oil and water will be pressed from the meal. Martin (1939) endeavours to prove theoretically that presses can never be expected to remove all the water and oil from a press-cake. He claims that, in the centrifugal

FIGURE 38. Continuous press (Courtesy California Press Mfg. Co.).

separation of oil and water from a meal, no extreme packing of the latter takes place, and therefore a greater yield of oil and water is obtained. This is only partly true. It must be remembered that the pressed meal still contains colloidally-bound water, and more important still, from the standpoint of oil yield, the protein material will still retain a certain quantity of oil through forces of absorption and/or adsorption. On several occasions the writer has had the opportunity of examining meal that has been subjected, whilst hot, to centrifugal action in various types of centrifugal separators. The oil content of these meals was of the same order as that in meals produced by pressing. Harrison (1931) has had similar experiences. Nevertheless, continuous centrifugal separators may be designed that have desirable features. Certainly, in such machines much of the fine protein material, now lost, would be recovered. A few years ago Ernest Scott and Co. of London, England, kindly furnished the writer with a description of a centrifuge with which they were experimenting. This machine is designed to eliminate presses and settling tanks and takes the cooked material straight from

the cookers. The centrifuge is of the horizontal type and is continuous. The cage is a solid one, driven by a 15 h.p. motor. The cooked mass is introduced whilst the machine is in motion, and the oil is continuously removed, as it is separated, by means of a decanting pipe which is controlled from outside the machine. When it is desired to remove the solid material from the centrifuge a knife is brought into action which detaches the mass from the cage. The distance of the knife from the cage of the centrifuge can be controlled with accuracy. The process consists simply in introducing the material, centrifuging, decanting the liquid and stripping out the residue. The meal may then be treated in a solvent extraction plant if the oil content is to be further reduced. A sample of herring oil made by this process has been examined in these laboratories and found to be of excellent quality. The writer has not had the opportunity of examining operating data for this separator, but no doubt these could be furnished by the manufacturers.

In connection with continuous fish meal and oil plants, an interesting description of the process for making oil and meal from herring in Iceland is given by Ludorff (1937). This writer states that fresh herring are not suitable for the production of meal and oil, as the latter is hard to press from the cooked material and that which is pressed out is emulsified. The herring are therefore placed in big bins 50 metres square and about 4 metres deep (approx. 150 feet square and 12 feet deep), and sprinkled liberally with ordinary salt. The bottom of the bin is sloping so that any oil liberated during the salting process can be removed and sent to storage tanks. The herring are left in these bins for 10 to 14 days, after which they are cooked and pressed in continuous plants as described above. Even though bacterial action may be stopped by this salt treatment, enzyme activity certainly goes on, and it is not surprising that herring oils produced by this method are higher in free fatty acids than those made from the fresh material.

(iii) SOLVENT EXTRACTORS, GENERAL PRINCIPLES

In considering a design of extraction plant for the removal of oil from any oil-bearing material, certain data are required regarding the nature of the material. Assuming that the type of solvent has been chosen, the first question to be considered is the form in which the material is to be extracted. Usually whole fish, fish offal or fish livers are first sterilized by heat, and a certain amount of the water removed by evaporation, or in some cases, more simply by allowing the material to drain after the sterilization has been completed. The amount of moisture requiring removal depends largely upon the type of material and the solvent used. The exact point at which to apply the solvent can be determined only by experiment. For instance, in Great Britain it has been found that offal from kippered herring can be handled in a solvent extraction plant after a short treatment in a steam-jacketed cooker. On the other hand, whole herring have to be cooked in a vacuum cooker until the moisture content has been reduced to about 25 per cent. In treating such fish as the bream, the fish are macerated and treated with a solvent in the raw state, which removes most of the water and takes out

the oil. The meal is freed of solvent and sterilized at the same time by treatment with steam. It is obvious, therefore, that each kind of material will require its own special technique.

When the proper conditions for treating with the solvent have been ascertained, there remains the question of the actual plant design. It must be remembered that, when a solid is extracted with a liquid solvent, a certain amount of entrainment of the solution in the solid will always take place. This entrainment will not necessarily remain constant as the extraction proceeds. Furthermore, in the interests of economy, it is always desirable that the solution of solvent and oil going to the solvent recovery plant should be as concentrated as possible. Ravenscroft (1936), in an excellent article, gives graphical solutions of problems involving multiple and continuous counter-current extraction and includes the case of extraction with varying entrainment. This author gives a practical example of the solution of the problem of the extraction of halibut livers with ethyl ether. Taking as a charge per extractor, 100 pounds of sterilized granulated halibut livers, it was found that 5.7 gallons of ether were required. Separation of menstruums of over 70 per cent of oil by volume from the liver mass was found to be too slow, and 65 per cent oil by volume was finally chosen. Using the batch counter-current principle, it was found that 4 or 5 extractors were necessary. The installation of a battery of 5 extractors was found, in actual practice, to give 98 per cent recovery of the oil.

Eddy (1931) gives some pointers in the design of solvent extraction plants, based on experience with a large commercial solvent extractor for vegetable oils. He suggests that, for the economical operation of a solvent recovery system: (1) a counter-current extractor of the simplest kind to wash out the greatest amount of oil with a minimum of solvent should be used, (2) only the most concentrated solutions feasibly obtainable should be distilled, (3) solvent recovery from the meal should be done in apparatus especially designed for the purpose and it should be used continuously so as to conserve steam consumption, and (4) a gas tight system with a good solvent recovery plant is essential for minimum solvent requirements. Werth (in Hefter-Schönfeld 1936) gives a comprehensive survey of the systems used for the solvent recovery of fats and oils from plant and animal materials. This treatise should be consulted by those interested in a detailed knowledge of the subject.

(iv) SOLVENTS

A suitable solvent for oil extraction should have a low boiling point in order that the meal and oil be not damaged during the removal of the solvent. It should be non-inflammable, easily purified, and should have a low latent heat of evaporation and a low specific heat. In addition, such a solvent should be non-toxic and without chemical action on the plant. Finally, the solvent should be cheap and available in large quantities. Some properties of a few solvents used in the commercial extraction of oils are given in table XXXIV.

Petroleum spirits are cheap but highly inflammable. Ethyl ether is inflammable, expensive, and fairly soluble in water. Acetone is used in some systems

in which the solvent acts as a dehydrating agent. The chlorinated hydrocarbons have become very popular, chiefly on account of their non-inflammable nature. Of these, trichlorethylene has proven to be the most satisfactory. The commercial product is a pure substance with a boiling range of only 1 degree, so that there is no high boiling residue left behind in the extracted material. Carlisle and Levine (1932) showed that trichlorethylene is very stable under practical conditions of use. This solvent is relatively non-toxic, has a great solvent.power for fats and oils and is itself only slightly soluble in water. Trichlorethylene has become one of the most important solvents for fat extraction. Detailed properties of this and other chlorinated hydrocarbons are given by Converse (1938).

TABLE XXXIV. Properties of some commercial solvents

Solvent	Boiling point range (°F.)	Specific gravity	Specific heat	Latent heat of evaporation (cal.)	Solubility of oils	Solubility of water per 100 cc.
Petroleum spirits...	140–248	0.67–0.70	app. 0.4	app. 76	Good	0.007
Benzene..........	176	0.88	0.41	93	Good	0.08
Ethylene dichloride.	176–187	1.25	0.30	88	Good	0.87
Trichlorethylene....	188–190	1.47	0.22	57	Good	0.01
Carbon tetrachloride	170	1.46	0.20	47	Good	0.08
Ethyl ether........	95	0.73	0.53	90	Good	7.5
Acetone..........	131–135	0.79	0.50	124	Fair	Miscible
Dioxane..........	214	1.03	....	..	Good	Miscible
Carbon disulphide..	116	1.29	0.25	90	Good	0.2

If a solvent is to be chosen for the extraction of an oil for industrial or medicinal purposes, at least four criteria should be considered, viz. (1) the wetting effect on the material to be extracted, (2) the solvent power for the oil, vitamins and undesirable non-oily constituents, (3) the stability of the vitamins in the solvent, and (4) stability of the vitamins during distillation of the solvent. No definite rules can be followed, as each material to be extracted presents a problem of its own. However, the following observations may be of some interest.

Wet uncooked material is difficult to extract, but the process is more efficient when carried out with solvents that are slightly soluble in water. In this case, ethyl ether and ethyl acetate are better solvents than petroleum spirits or chlorinated hydrocarbons. For wet cooked material the same is true, but in this case the latter two solvents give slightly higher yields than with the uncooked material.

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With dry materials, the wetting and penetration by all solvents is very rapid, but even in this case there is a measurable difference between various solvents. W. A. Riddell (1934) reports that from dried oily fish the rates of "oil" extraction by various solvents decreased in the following order: chloroform, acetone, petroleum spirits, ethyl ether, ethylene dichloride and carbon tetrachloride. Harrison (1938), however, found that acetone was much slower than other solvents in extracting oil from dried fish meal.

The total amount of material extracted by a given solvent depends upon the nature of the material. Working with cod livers dried with sodium sulphate, Pugsley (unpub.) found that, with the exception of acetone, practically all solvents gave the same yield of oil during cold extraction. Under identical conditions acetone gave yields some 10 per cent lower. The vitamin potency of all the oils was the same. Commenting on the yields of solvent extractable material obtained from dried fish meal, Harrison (1938) says: "From the standpoint of gross extraction, the supposedly aliphatic petroleum hydrocarbons gave the lowest values, and these in general increased with boiling temperature. Ethyl ether, carbon bisulfide and cyclohexane gave quite similar values, slightly above petroleum ether, hexane and heptane." In addition to the true fats or oils, tissue material contains other fat-solvent extractables, such as phospholipides, sterols, higher alcohols, pigments, etc. The amount of these materials extracted will depend to some extent upon the nature of the solvent. For instance, Stout, Schuette and Fischer (1934) found that there was considerable difference in the nature of the oil extracted from rye embryos, depending upon the nature of the solvent used. Acetone and chloroform gave the highest yields, and ethyl ether and petroleum spirits the lowest. Carbon bisulphide gave the highest yield of unsaponifiable matter and chloroform the lowest. High yields of phospholipides were given by chloroform, benzene and ethylene dichloride, medium yields by carbon bisulphide and carbon tetrachloride and low yields by petroleum spirits, ethyl ether and acetone. Colour also varied considerably, the darkest oils being obtained with carbon bisulphide and ethylene dichloride. For a more detailed account of the properties of these non-oily constituents, the reader should consult Section 3 of this Bulletin.

Solvent extracted oils are usually darker in colour than those obtained by pressing. Of the factors affecting this colour, the type of solvent used is by no means the most important. The freshness of the material, the amount of oxidation the oil has suffered prior to extraction, and the actual oil content of the material all have an important bearing on the colour of the final oil. Temperature of extraction is also important; the higher the temperature the darker the oil. Those solvents that form peroxides or other labile oxygen compounds are prone to darken the oil through oxidation, prior to and during distillation, e.g. ethyl ether and acetone. Some of the chlorinated hydrocarbons liberate hydrochloric acid in the presence of moisture at high temperatures, and this also may cause a darkening of the oil. The solvent chosen, therefore, should be stable for the conditions under which it is to be used.

In regard to the stability of vitamins in solutions of extracted oils, that of vitamin A is of most importance. Pugsley (unpub.) found that an oil, containing 3,500 units of vitamin A per gram, lost 90 per cent in chloroform, 34 per cent in ethyl ether, and only 5 per cent in petroleum spirits after a period of 4 days at room temperature and in diffused daylight. The loss during distillation of these solvents is of the same order. The stability of vitamin A in any solvent is clearly associated with the stability of that solvent. Distillation in an inert atmosphere or under reduced pressure considerably reduces loss of vitamin A during concentration of the oil.

(v) BATCH-TYPE SOLVENT EXTRACTORS

These extractors are made in both horizontal and vertical styles, with or without mechanical agitation. The horizontal extractors are made either in the stationary or in the revolving types. The stationary kinds usually are equipped with stirring paddles, whilst the revolving extractors depend upon the rotation of the cylinder for agitation. Both types are jacketed for steam or hot water, and are arranged so that the solvent can flow continuously or intermittently through the extracting cylinder, and from there to the solvent recovery plant. Many rotary extractors are made with self-contained strainers so that the oil-solvent solution may be treated directly in the solvent recovery plant. This type of extractor is most suitable for material that is dense and moist.

Vertical solvent extractors are also made with and without agitators. In the former types the material is supported on perforated baffles and the solvent is allowed to percolate through the material. Obviously, only coarse dry material can be treated by percolation. The simple percolating type solvent extractor, shown in figure 39, is arranged for the extraction of oil from coarse materials by the continuous percolation of trichlorethylene. The extractor is not jacketed, and dry steam is used for the elimination of the last traces of solvent from the meal. The solvent is recovered from the oil by vacuum distillation. A semi-continuous solvent plant is shown in figure 40. In this plant dry material, even when finely divided, can be treated by the percolation process. The material is charged into the percolating tubes (A) of which there may be from one to four, depending upon the capacity of the plant, where the material is treated with warm solvent, which in this case is petroleum benzene (b.p. 90 to 110°C., 194 to 230°F.). The solvent containing the dissolved oil is withdrawn through a specially constructed valve (B), the upper part of which is perforated, thus allowing the liquids, but not the solids, to pass out to the recovery plant. The lower part of the valve closes off the drying vessel (C) immediately underneath. The plant is semi-continuous, for, whilst the fish meal is being extracted in the percolating tubes above, the extracted material of the previous charge is being subjected to dry heat and vacuum in the drying vessel below. The solvent recovered from the drying vessel and from the solvent recovery plant is then re-circulated through the percolation tubes.

A solvent extraction plant of the batch type and utilizing vertical cylinders

equipped with stirring paddles is shown in figure 41. This plant is intended as an auxiliary to a fish meal plant to handle any oily fish that may be utilized. In the fish meal plant the fish are first hacked into small pieces and put through a preliminary sterilizer where the fish is treated with steam at 35 lb. pressure. From the sterilizer the meal goes through the steam-jacketed drier. Drying is effected by intimate contact with the jacket through which steam at 25 lb. pressure is passed. The number and size of these driers depends upon the capacity of the
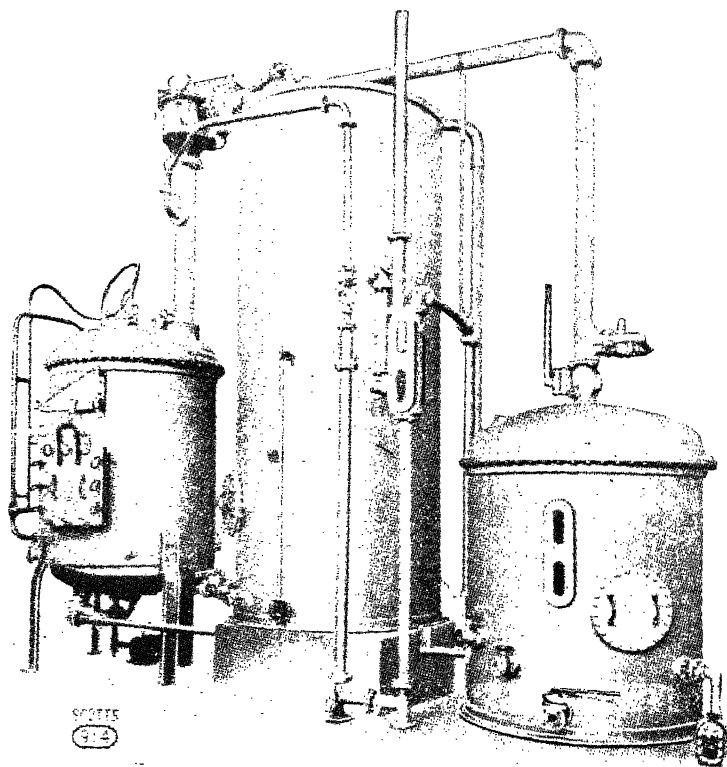
FIGURE 39. Simple solvent extraction plant—percolator type (Courtesy Ernest Scott and Co., London).

plant. In one installation four cylinders each 44 feet long and 3 feet in diameter are used. The fish meal takes approximately 2.5 hours to pass through these four drying cylinders. If the fish meal is of the oily type, it is now delivered by a screw conveyor to a bin above the solvent extraction plant, where it is fed into the vertical extractors by means of movable chutes. Hot solvent (trichlorethylene) is admitted into the extractor by means of valves which are so arranged that the solvent can be admitted at either the top or the bottom of the vessel.

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When the solvent becomes saturated with oil it is passed through filters into the distillation unit. The apparatus can be utilized so that only saturated solvent is finally distilled. Solvent remaining in the extracted meal is removed with live steam, after which the damp meal is dried in an "after" drier similar in design to the original steam driers. This type of equipment is in general use where the bulk of the material handled is non-oily, but where oily material is sometimes processed. The solvent extraction part of the plant is, therefore, usually of small capacity.
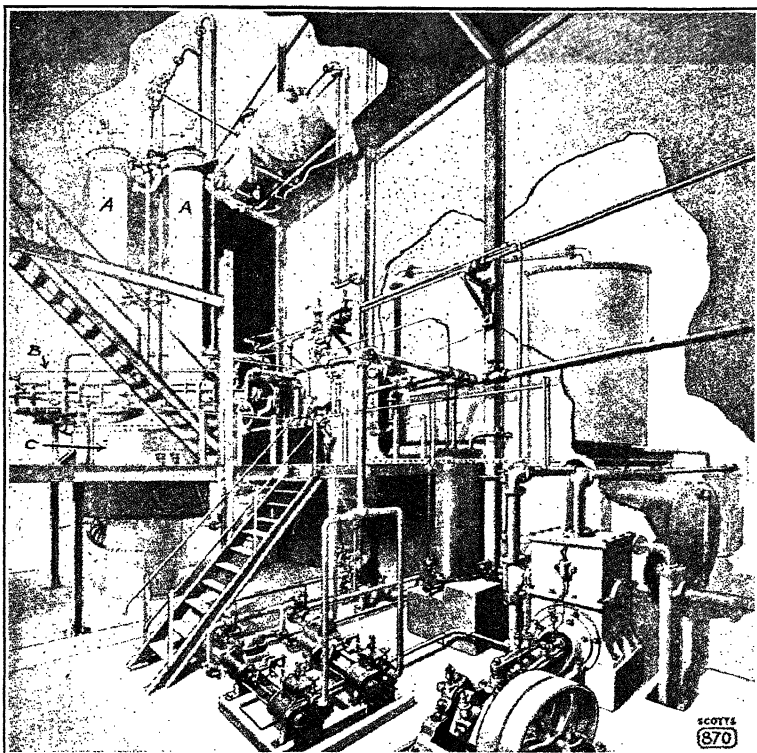
FIGURE 40. Semi-continuous solvent extraction plant, percolating system (Courtesy Ernest Scott and Co., London).

A solvent fish meal and oil plant of the batch type, designed to extract the raw material in the wet condition, is shown in figure 42. This plant utilizes acetone as solvent, which first dehydrates the sterilized material and removes any free fatty acids present in the oil, and finally dissolves out practically neutral oil. The operation of this plant is as follows: The fish are delivered into the sterilizing macerator A where they are heated to 100°C. and disintegrated. The hot material then passes to the rotary jacketed extractor B. These extractors are about 14 feet long and 7 feet in diameter and hold 5 tons of material at one charge. One or more are used depending upon the total capacity of the plant. The material is rotated in the presence of a charge of acetone at a temperature of 60°C. After the preliminary extraction is complete

the extractor is stopped and the solution of dilute acetone and free fatty acids is run out by means of built-in filter pipes. This solution runs to receivers C and from there to a still K, where the greater part of the acetone is recovered. In the meantime, the solid material in the extractor B is treated with a further charge of the solvent, which this time removes the remainder of the water and a greater amount of oil, since the solubility of the oil increases as the water content of the acetone decreases. This solution is removed to another still and a further charge of acetone run into the extractor. Extraction is repeated until the material has been sufficiently de-oiled. Usually three extractions suffice. The recovery still, handling the first extract, is of slightly different design from that used for the subsequent solutions, since the preliminary extract contains a large amount of water, some free fatty acids and salt. Subsequent solutions contain practically only oil and some water. The solvent is removed from the oil under reduced pressure. The solid material remaining in the extractor is freed from solvent by indirect heat, steam, and finally by heating under reduced pressure.
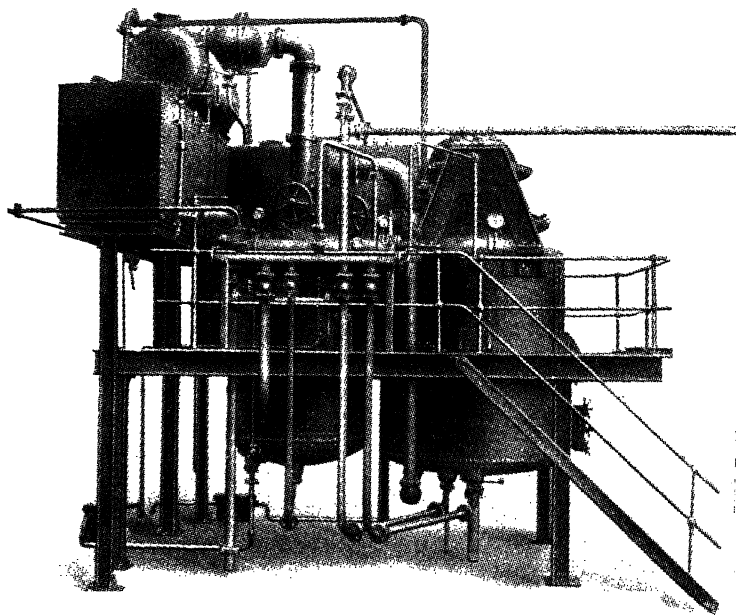
FIGURE 41. Self-contained solvent extraction plant for oily fish meal (Courtesy Rose, Downs and Thompson, Ltd.).

Samples of oil and meal made by this Wilhelm process have been examined in these laboratories and were found to be of excellent quality. The oil, made from whole herring, was of a light yellow colour and free from suspended material. It had a very low free-fatty-acid content. Usually, with fresh herring, acidities of the oil run less than 0.5. The meal contains from 1 to 1.5 per cent fat.

It has been suggested that this type of plant might be suitable for use in conjunction with the continuous-press plants where fish meals of low oil content are desired. By taking the meal direct from the presses, where the water content has been reduced about 50 per cent, less acetone would be required to dehydrate the meal than if the raw material were treated. The oil produced from this

pressed material by acetone extraction is of the same quality as that obtained by the settling tank system.

(vi) BATTERY-TYPE SOLVENT EXTRACTORS

In some large European establishments the counter-current principle of solvent extraction is practised by the use of a battery of unit extractors, so arranged that the solvent of highest oil concentration treats material with the highest oil content. The process is continuous in that one extractor unit is disconnected from the solvent line for removal of and filling with the meal, whilst extraction continues in the other units. Battery extractors are usually of the horizontal type and are fitted with paddles and steam jackets. The process has been used principally in the extraction of oil from seeds, but has been recommended for dry oily fish meal.

FIGURE 42. Wilhelm extractor.

(vii) CONTINUOUS-SYSTEM SOLVENT EXTRACTORS

A great variety of designs in continuous solvent extraction plants is available. Most of these are of Continental origin and were originally intended for the solvent treatment of oil-containing seeds of various kinds. Some of these plants have been adapted for use in fish meal and oil production. In all of them the macerated material is passed continuously counter-current to the solvent. The variations in design have to do largely with the mechanical features of the plant, such as the mechanism of moving the material in the extractors, and the method of treatment of the material prior to extraction.

In Brit. patent 156,905, Bollmann describes an apparatus in which the material is fed into trays that pass on a continuous belt over two wheels arranged vertically one above the other. The material is fed into the trays at the top, and on the way down is sprayed with solvent with-

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drawn from the bottom of the extractor and containing some dissolved oil. On the way up, however, the material is thoroughly flushed with fresh solvent. The extracts from the two sides of the apparatus are kept separate, that collected during the upward spraying being used over again for the downward spraying, after which it is pumped to the solvent recovery plant.

In a patent issued to Mills and Battle (Ger. patent 237,497), the coarse ground material is forced into a long vertical cylindrical extractor through a side arm where it is carried upwards
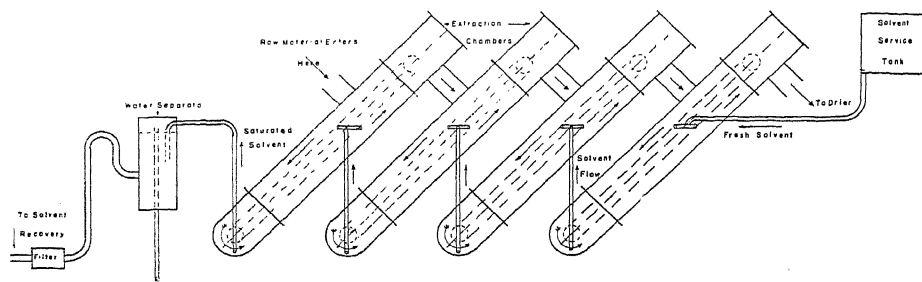
DE-OILING SYSTEM
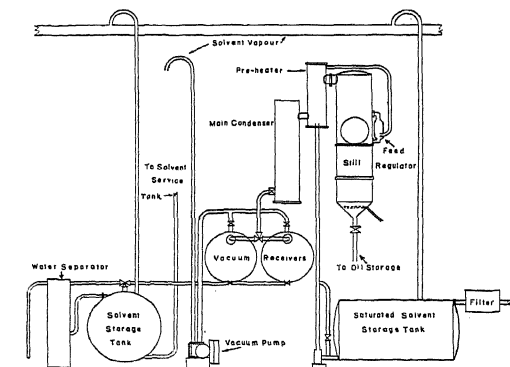
SOLVENT RECOVERY SYSTEM

FIGURE 43. Continuous solvent extraction plant. Sterling patents (Brit. 286,752).

by paddles, and removed at the top by means of a spiral conveyor set into the extraction cylinder at a slight angle. Solvent is run in at the top of the cylinder and is removed at the bottom through a screen. The screw conveyors are steam-jacketed, and the residual solvent in the meal is removed whilst passing along to the discharge outlet. Many other methods of conveying the material through the solvent have been patented. In a patent taken out by Schlotterhose and Co. (Fr. patent 679,226), the material is conveyed through a series of tubes, inclined at an angle of 45°, by means of spiral screws. When the material reaches the top of one inclined tube it falls into the

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lower end of the next one. In the meantime the solvent flows through the tubes in the opposite direction. The upper part of each inclined tube is tapered in order to squeeze out a portion of the solvent before the material progresses into the next tube.

A British-made continuous solvent extraction plant patented by John Sterling, Ltd. (Brit. patent 286,752), and designed especially for fish meal and oil production, is shown in essential outline in figure 43. The raw fish is first fed into a crusher and then elevated into the first of a series of inclined extraction cylinders in which warm solvent (trichlorethylene) is fed on the counter-current principle. The material passes down one side of the cylinder and up the other by means of a bucket-type conveyor. The partition down the centre of the cylinder is in the form of a jacket through which steam or hot water can be circulated. The material progresses from one cylinder to another. Clear warm solvent is fed into the last cylinder so that the material leaving the extraction apparatus gets a final wash with pure solvent. The solution from the first extraction cylinder is pumped to the solvent recovery plant where the solvent is removed from the oil by vacuum distillation. The de-oiled meal passes into a drier-cooker where it is cooked, freed from absorbed solvent, and dried in one operation.

In this process it is to be noted that the material to be de-oiled is treated in the raw state with a water-immiscible solvent. This solvent removes, mechanically, a quantity of water which is separated before the solvent enters the vacuum still. The makers of this plant claim that excellent extraction of the oil is obtained and point to the fact that the efficient removal of the oil from the raw material is due to the extraction taking place whilst the material is being heated. This plant has received much commendation from scientific investigators, particularly those interested in the production of a fat-free fish meal for animal feeding.

(viii) CENTRIFUGAL SOLVENT EXTRACTORS

Werth (in Hefter-Schönfeld 1936) describes two Continental-designed solvent extracting centrifuges which illustrate the possibilities of this type of extractor. The earlier model, due to Strehlenlert (Ger. patent 150,158), has a perforated bowl rotating inside a fixed casing. The bowl is filled with the material to be extracted and both the bowl and casing are then flooded with the solvent. As the perforated bowl rotates, the material is thrown against the perforated side, and the solvent is thrown up the sides of the outer fixed casing. As the solvent builds up the side of the casing, it is deflected back into the centre of the rotating bowl and thus passes continuously through the material. When extraction is finished, the solvent is allowed to flow out of the bottom of the casing and the material centrifuged until most of the remaining solvent has been removed.

Steinmann's extracting centrifuge consists of a squat bowl divided into three concentric compartments. The outer compartment is divided from the middle compartment by a perforated wall. The centre compartment contains only the solvent-collecting pipe fixed in the solid centre wall. The material to be extracted is placed in the middle compartment and the solvent is fed into the outer compartment by means of feed pipes that rotate with the bowl. The solid material is thrown against the perforated wall but, owing to the centrifugal force, the solvent is forced from the outer compartment through the solid material and is sucked out through the collecting pipe in the centre compartment. The solvent may thus be automatically returned through the material or led away to the recovery still. The advantage of these types of extractors lies in the positive circulation of the solvent through the solid material, and in the centrifugal removal of most of the entrained solvent after extraction has been completed.

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(ix) SOLVENT RECOVERY SYSTEMS

A detailed treatment of this subject is beyond the scope of this Bulletin, and the following brief outline must suffice. Before pumping to the solvent recovery plant the oil-solvent solution is first filtered to remove any finely divided solids. In the recovery plant the solvent is distilled off as rapidly as possible, and at the lowest feasible temperature. Both batch and continuous solvent recovery stills are used. The former are obtainable in horizontal and vertical models and the solution is usually heated by means of steam coils at the bottom of the still. Many designs are available with heating units similar to fire-tube boilers; the solution passes through tubes arranged in a steam chest, and by suitable baffles a rapid circulation of the solution is effected.

In the continuous types of stills the oil-solvent solution is allowed to trickle down over heated baffle plates. The design of these plates is the subject of a large number of patents. Usually the solvent is practically entirely removed by the time the oil reaches the bottom of the apparatus. In most plants, it is customary to remove the last trace of solvent from the oil by direct treatment with slightly super-heated steam. Such treatment effects considerable deodorization of the oil.

Distillation of the solvent under reduced pressure has many advantages, but has not been generally adopted as yet. Equipment for reduced-pressure distillation or evaporation is complicated, particularly with regard to the treatment of the solvent-saturated vapour emanating from the vacuum pump. Even with the most efficient condensing systems much solvent vapour passes through the pump, and in modern installations is usually recovered by adsorption systems using activated carbon or silica gel. The tendency in modern solvent oil recovery systems, however, appears to be towards the use of reduced pressures during distillation. Sterling's plant mentioned above under (vii) is a typical example.

(e) WHALE BLUBBER, FLESH, ETC.

In the earlier days of the whaling industry only the blubber was used as a source of oil. This was usually rendered in large open kettles with live steam, and the process required from 10 to 12 hours. Only about 80 per cent of the total oil could be recovered by this process, and it is gradually being replaced by pressure cooking. The open steam rendering process, whilst slow, yielded a bright clear yellow oil and it must be admitted that the newer, more efficient methods do not produce quite so light a product. The long cooking time required by the open steam method was due, in part, to the fact that no suitable apparatus for disintegrating the blubber could be found. Rotary hashers were and are being used, which cut the tough blubber into pieces about $6 \times 6 \times 3$ inches. Recently, however, blubber presses have been introduced which consist essentially of heavy corrugated rollers, which handle about 6 tons per hour. Passage through two sets of these presses converts the blubber into a semi-fluid brei which can be rendered more quickly than the blubber in the form of lumps. It is claimed that

the time of rendering can be reduced to less than half by the use of these heavy presses.

The high pressure digesters which are being quite generally adopted are made in both vertical and horizontal types. The vertical types may be from 12 to 18 feet high and from 6 to 9 feet in diameter. They are built to stand pressures of 4 to 6 atmospheres and will render a charge in from 2 to 16 hours, depending upon the material. These digesters are usually built with suitable strainers to remove whale vertebrae and other debris from the oil. The latter, along with the "stick-water", is withdrawn periodically through stop-cocks in the side of the digester, so that the oil is not unduly subjected to the high pressure. The oil and "stick-water" then pass to the separatory system.

The horizontal type of digestor is usually semi- or wholly continuous and is gradually replacing all other types. A typical design of one of these digestors is shown in figure 44. The blubber, cut into small pieces, is fed into the sluices A and A^1 where, through an automatic opening device, it falls into the pre-heater B and B^1. In this pre-heater, the blubber is subjected
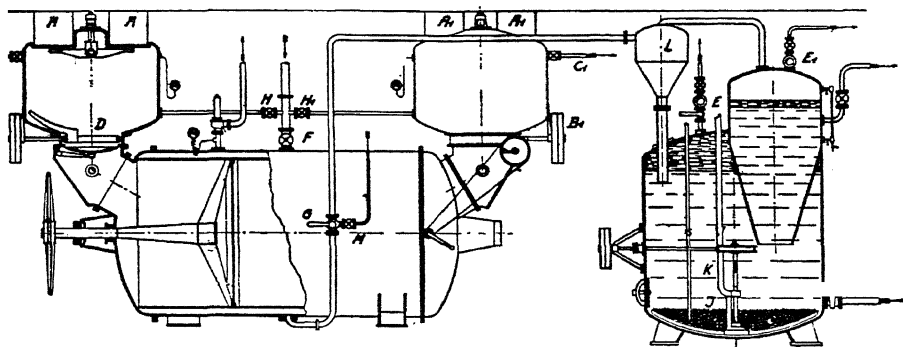
FIGURE 44. Horizontal whale blubber digestor.

to open steam. The valve leading from the pre-heater to the extractor is automatically opened when the pressure in the pre-heater becomes greater than that in the extractor. The extractor itself consists of a heavy iron tank inside which rotates a perforated drum fixed to a heavy shaft. The perforated drum is open at both ends and the material from the pre-heaters is fed into each end whilst the drum is rotating. The action of the high pressure and temperature, plus the grinding action of the drum as it rotates, releases the oil and water and converts the solid portion of the blubber into a fluid brei. The mixture of oil, water and brei, forced through the perforated drum to the bottom of the extractor, is continuously removed through an outlet pipe at the bottom, working through a suitable pressure valve. When the pressure in the extractor falls below that in the pre-heater, the contents of the latter are automatically dumped into the extractor, thus renewing the charge. The mixture of oil, water and brei is forced into the separator tank where most of the water and solid material is removed by gravity.

Digesters for whale flesh and bones are similar in construction to those used for the blubber, with the exception that the pre-heaters are not generally used. Suitable straining equipment is provided to remove larger pieces of bone, after which the cooked material goes to continuous presses where the oil and water are

removed from the solid protein material. The former then pass to the gravity separator and the latter is dried in continuous driers for use as an animal food.

The most advanced designs in whaling establishments are found in the large mother ships now operating in the Antarctic. In these floating factories every part of the process is continuous. It is of interest to note the treatment of the whale oil after it has left the gravity separator. In most installations the partly clear oil is pumped to a separator room where it is put through a coarse and then a fine filter, prior to removal of the last traces of water and solid material in centrifugal separators. These separators are usually run in groups of from 4 to 8 machines, and great care is taken that sufficient capacity is available, since space is at a premium and there is no room for extra tank space for unfinished oil. The finished oil is run directly into storage tanks in the hold of the vessel. Provision is made for keeping the various grades of oil separate.

II. SEPARATION OF OIL FROM PRESS LIQUORS

In plants producing fish meal and oil by the pressing process the oil is usually separated from the wet meal as a mixture of oil, dissolved nitrogenous material and finely suspended protein particles. In many cases this mixture is emulsified and a preliminary breaking of the emulsion must be effected before the oil can be finally purified and sent to storage. In solvent recovery systems steam is usually used to drive off the last trace of solvent from the oil, and the water must be removed before storing the oil. The following account of the methods used to accomplish the above processes is by no means exhaustive, but will suffice to indicate the principles of the various methods suggested or in actual use.

(a) GRAVITY SETTLING SYSTEMS

(i) NATURE OF EMULSIONS

When a mixture of pure oil and water is shaken, an unstable emulsion is obtained consisting of oil globules dispersed in the water. Separation into two layers takes place because of the tendency of the oil globules to coalesce and thus form a smaller total surface area. The rate at which the oil separates depends upon the viscosity of the water, the difference in specific gravity between the oil and the water, the relation between the mass and the surface area of the oil globules and, finally, the temperature. Raising the temperature reduces the viscosity of the water and thus allows of a more rapid separation.

The nature of the interface between the oil globules and the water is of the greatest importance as regards the stability of the emulsion. In a simple oil and water emulsion, the oil tends to form large drops because by so doing the total interfacial surface energy is reduced. If, however, a water soluble substance that reduces the surface tension of the water (e.g. soap solution) is added, this third substance becomes concentrated at the interface between the oil globules and the water, forming a so-called "skin" around the globules. Actually, the third substance at the interface between the oil and the water is orientated in

such a manner that the part of the molecule that tends to dissolve in the oil is attached to the globule, and the part that dissolves in the water is immersed in the surrounding water. The final effect is to reduce the interfacial surface tension between the oil globules and the water so that there is less tendency for the globules to coalesce.

A material that stabilizes an oil-in-water emulsion must be colloidal in character and must be soluble in, or wetted by, water. In press liquors the materials that may act as stabilizers are, in order of increasing importance, finely-divided solids, ammonium soaps of the fatty acids and dissolved proteins. In press liquors produced from the fresh material, the dissolved proteins are probably exclusively responsible for the stabilization. In liquors from partly decomposed material, free fatty acids and soaps also add to the stabilizing effect. Finely-divided solids are usually always present, but their role as stabilizing agents appears to vary with the freshness of the material. The removal of such particles certainly assists in breaking the emulsion.

To break an emulsion the stabilising material must be either removed, or so treated as to lose its colloidal character, and/or the emulsion must be processed in a centrifuge. Where soap alone stabilizes an emulsion, the latter may be broken by adjusting its acidity to the point where the soap is decomposed, or the mixture heated to a temperature where the soap loses its colloidal character and becomes a true solution. Protein material that stabilizes is usually more difficult to deal with. Coagulation or denaturation by heating is sometimes partially effective, but the results of this treatment vary considerably with the nature of the emulsion. Usually some chemical treatment is necessary, either to remove the protein entirely, or to destroy its colloidal properties. In coagulating stabilizing protein, salts are usually used and the conditions under which they are added is of some importance. If the salt is added to a *neutral* solution or mixture, then its addition gives a "salting-out" effect, and the amount of protein precipitated is a function of the final salt concentration. In other words, a high concentration of salt is required before any noticeable effect is obtained. If, however, the mixture contains a little acid or alkali, then the proteins behave quite differently, and are precipitated with relatively small concentrations of salt, the actual concentration necessary depending upon the valency of the metal. Thus magnesium sulphate is more effective than sodium sulphate, and aluminium sulphate is much more effective than magnesium sulphate.

Undoubtedly the most satisfactory method of treating emulsions is by centrifuging. This is particularly true where the solids content of the press liquor is low. By proper chemical treatment prior to centrifuging, even the most obstinate emulsions can often be handled by a centrifuge, where otherwise the oil contained in such an emulsion would be lost. Designs and uses of centrifuges are discussed more fully in a later part of this section.

(ii) BREAKING TANKS AND SETTLING SYSTEMS

Gravity oil recovery systems consist essentially of a heated breaking tank and a series of settling tanks which may or may not be heated. The design and

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arrangement of these tanks vary with practically every installation, as does the mode of operation. However, the systems can be described as following three general types, two of which are continuous and one intermittent.

In figure 45 are shown in outline the essentials of the continuous settling system largely used on the Pacific coast for the separation of oil from pilchard, herring, sardine and salmon press liquor. The tanks A, B, C and D are arranged so that the overflow from the higher tank can run into the next lower one. The description of this system as given by Beall (1933) is as follows: "All the tanks are fitted with steam coils to regulate the temperature and have a capacity of 1200 gallons each. Each tank tapers at the bottom and has an outlet valve to allow draining. Usually all the separating, i.e. breaking of the emulsion, is done in the tank A. The press liquors enter by the pipe E and by means of an adjustable spout are delivered into the tank 12 to 18 inches below the level of the overflow F. In this way the surface of the liquid is kept still and the oil has an opportunity to rise. The remaining liquors, after the oil has risen and passed into tank B,
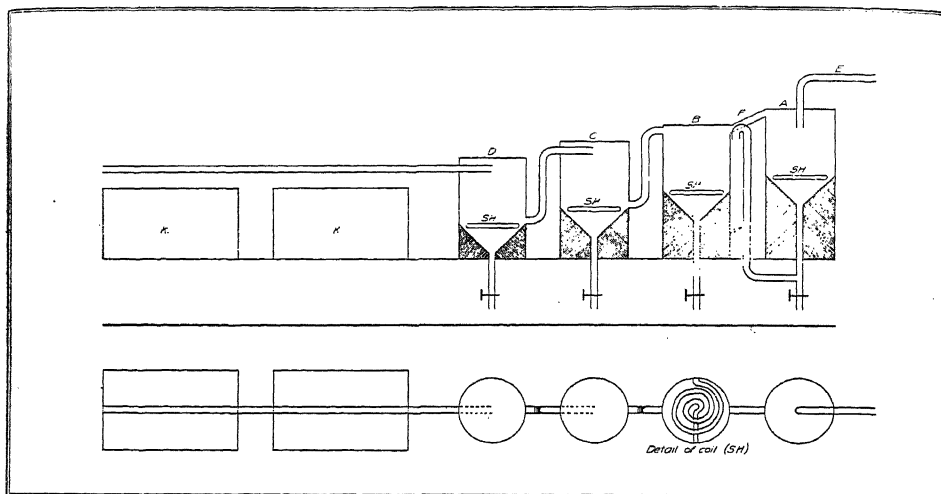
FIGURE 45. Diagrammatic representation of equipment used in separating oil from aqueous fraction of press liquors.

pass out of the pipe M. This is adjustable in height and by means of it the depth of the oil in A is controlled and hence the time the press liquors remain in tank A. The tanks B, C, and D are really purifying tanks, the oil passing from B to the bottom of C, which is half full of water, and the process is repeated from C to D. It then passes along pipe I to the cooking tanks where it is heated for about $1\frac{1}{2}$ hours to allow any solids to settle. After cooking the oil is pumped to storage tanks. If, as sometimes happens, the fish are old or contain certain types of feed, the oil can be separated only with considerable difficulty and at such times both A and B are used as separating tanks."

In this system the object is to break the emulsion in the first or second tank, and the mixture passed on to the third and fourth tanks consists of oil and "stick-water" mixed with a considerable amount of finely-divided solids. This mixture readily separates and the object now is to remove the finely-divided solids that are dispersed throughout the oil. Some operators prefer to heat the oil from

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which the "stick-water" has been removed, giving it a final "cook", during which time most of the solids separate. The danger of this practice is that, should the solids be hard to separate, a long "cook" is necessary, and in the presence of the solids such a treatment darkens the oil considerably. Other operators prefer to settle out the solids by passing the dirty oil into tanks containing considerable fresh water. The mixture is gently heated and the water washes out the solids. This procedure is followed in each of the settling tanks up to the last, where the oil, now tolerably free of solids and "stick-water", is heated to dry it before it passes to the storage tanks.

The intermittent type of settling tanks used on the Pacific coast consists of one large tank, for breaking and partial purification of the oil. The press liquors are run directly to this tank where they are heated by means of closed steam coils for periods up to four hours or more. The oil is allowed to separate, and is run to storage tanks whilst the remaining liquors may be dumped or pumped to another smaller breaking tank where they are further heated and settling is allowed to take place.

Separation of the oil from the press liquors in the menhaden industry by settling tanks is described in some detail by Harrison (1931). The equipment consists essentially of a series of settling tanks and smaller "cooking tanks". The settling tanks are equipped with end gates that permit direct overflow into the next tank in the series. In addition, each tank has a side gate or self-skimmer through which any free oil is automatically allowed to flow directly to the cooking tanks, and also a siphon box which extends to within about six inches of the bottom of the tank. This siphon discharges directly into the next tank or into any others in the series, and is used for the continuous removal of the liquors nearest the bottom of the tank. The cooking tanks are smaller than the separating tanks and are equipped with heating coils and a discharge pipe attached to a swivel joint and running through the base of the tank. By raising or lowering the pipe, the oil can be skimmed off without disturbing the bulk of the liquors.

Operation of the settling tanks is performed in two ways. If the liquors produced during an operation occupy not more than the total capacity of the settling system, they are allowed to flow from one tank to another without any attempt being made to skim off any free oil. Considerable separation takes place and the last tank is richer in oil than the first. The contents of the tanks are allowed to stand overnight. Water is then pumped into the first tank and the oil and emulsion floated from one tank to the next, the oil accumulating in the last tank being run out through the side gate into the cooking tanks. Here the oil and emulsion are heated for several hours, during which time the emulsion breaks and finely-divided solids separate out. The oil is then pumped to storage.

In the second method of operation the system is used on the continuous-flow principle, heat being applied to the first two or three tanks to assist in breaking the emulsion. In the tank where a good break is being obtained, the self-skimmer removes the clear oil from the top and the siphon box is put into operation to keep the volume of waste liquors, accumulating at the bottom of the tank, at a constant level. The skimmed oil goes to the cooking tanks where it is heated with steam and the solids allowed to settle. The waste liquor from the siphon box may be dumped, or, if containing enough oil, may be further treated. After the free oil in the cooking tanks has been pumped to storage there remain some emulsion and free water together with solid materials. This "gurry" is treated either by allowing it to rot for a few days and then reheating it, or it is put through filter presses using maple sawdust as a filter aid. The latter method, of course, gives the better grade of oil and in some plants no effort is made to get a close skim of oil during the settling process, the recovery in the filtering system being relied upon to maintain the oil yield.

Finally, some menhaden plants pump the oil from the cooking tanks to open cooling tanks

where the last traces of finely-divided solids and water have the opportunity of settling out before the oil goes to the storage tanks.

(iii) FILTERING AS AN AID TO SEPARATION

As mentioned above, menhaden operators have found that filtering "stick-water" through filter presses with the aid of maple sawdust sometimes aids in breaking troublesome emulsions. This treatment is applied to the small amount of emulsion left after the final heating or cooking process. However, several years ago it was suggested that filtration of the total liquors from the presses through a plate-and-frame type of press with the aid of diatomaceous filter-aids, would remove all the suspended solid material and allow a quick separation of the oil from the clear water. In actual practice this scheme did not work out so well. Flow-rates through the filter presses were much too slow and, even when filtered, emulsions were not necessarily broken. Direct mechanical filtration of the press liquors did not seem to be of any value unless they were given a preliminary chemical treatment.

A successful modification of the direct filtering process, made by Chas. F. Zoul, consists in passing the hot liquors from the presses through a specially designed, slowly revolving hexagonal screen, that removes a large portion of the suspended solids. The liquor from this screen is mixed with a special grade of diatomacous earth and pumped through an external channel-feed filter press, thus removing practically all suspended solids. The oil and water mixture is then passed to an ordinary settling tank where rapid separation of the oil takes place. The oil retained by the solid cake in the filter press may be recovered, either by blowing with air or by washing out with water. It is claimed that a filter press having 30 cells 30 inches square will handle 1,000 gallons an hour of the press liquor from the hexagonal screen, and the process appears to be meeting with considerable success in commercial installations.

(iv) CHEMICAL COAGULATION AS AN AID TO SEPARATION

Considerable work has been done on the chemical treatment of press liquors in an effort to speed up the breaking of emulsions and to increase the yield of meal and oil. Before considering some of these methods, it is desirable to record here the actual composition of some press liquors and "stick-waters" from pilchard and herring oil plants. The liquor from presses working on pilchards was found by Beall (unpub.) to consist of 14.8 per cent oil, 2.4 per cent dissolved protein and 0.9 per cent solid meal. After passing through a continuous settling tank system, an average sample of the "stick-water" showed 0.5 per cent oil, 2.9 per cent dissolved protein and 1.9 per cent solid meal. A sample of "stick-water" dumped from a settling-tank system operating on herring was examined by the writer as follows: 3.0 per cent oil, 1.4 per cent insoluble protein, 1.1 per cent soluble protein and 3.6 per cent of protein degradation products. The chemical treatment of such effluents usually effects some coagulation of the soluble proteins, and does not affect to any extent the nature or amount of the protein degradation products.

Taylor, quoted by Harrison (1931), investigated the effect of pH on the

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filtering properties of menhaden press liquors. He found that when acid alone was used, the maximum rate of filtering was obtained at about pH 4.2, but, when used in conjunction with aluminium sulphate, the optimum pH increased to about 4.4. Further investigation showed that aluminium or iron sulphate alone increased the filtering rate of such liquors to a marked degree. Taylor suggested the addition of 1 lb. of technical aluminium sulphate or 0.6 lb. of ferric chloride for each 12 gallons of press liquor and the use of a recessed-plate type of filter press. With a small experimental filter press the rate of filtration in gallons per hour per square foot of filter area was 0.8 for aluminium sulphate and 1.08 for ferric chloride. In addition to breaking the emulsion, the use of the above coagulants permits the recovery of practically all suspended solids and about one-third of the dissolved protein.

Beall (unpub.) investigated the effect of a few chemical coagulants on pilchard effluents. Alum did not appear to have any great effect on the breaking of the emulsion. Acid treatment, whilst variable in its effect, did bring about some coagulation of the dissolved and suspended protein. The effect was not large, and in addition, the coagulated material carried down with it considerable adsorbed oil.

Johnston (1938) evolved a process for the removal of suspended matter from the effluents of fish meal plants, which consisted in bringing the acidity of the effluent to pH 4, and then treating with formaldehyde and heat. The treatment requires about 25 lb. of commercial sulphuric acid and 25 lb. of formaldehyde (40%) per 1000 gallons of effluent. When applied to the effluent of Atlantic coast plants working on relatively non-oily fish, this method appears to effect a considerable saving in protein. Applied by the writer to the "stick-water" of a herring plant, however, the results were not so definite. A certain increase in the rate of breaking of the emulsion was noted, but the precipitated meal was finely divided and carried with it considerable oil. The particle size of the precipitated material was too small to allow of screening, and, should this method be tried in pilchard and herring reduction plants, it should be used in conjunction with a filter press.

(b) Centrifugal Systems

(i) principles of centrifugal separation of water from oil

In an oil-in-water emulsion the velocity at which the oil particles move through the water can be described by Stokes' law as $V = \dfrac{2r^2(s - s')g}{9\eta}$, where $V =$ velocity of the oil particle, $r =$ radius of oil globules, $s' =$ specific gravity of water, $s =$ specific gravity of oil, $\eta =$ viscosity of water, and $g =$ force of gravity. From this equation it is seen that, although the difference in specific gravity between the oil and water is important, the size of the oil globules is of still greater importance since the velocity is proportional to the square of the radius. Thus, very finely-divided oil globules separate at a much slower rate than larger particles.

The velocity of separation is also inversely proportional to the viscosity of the water or watery phase, and directly proportional to the gravitational effect. Of all the factors in this equation, that of gravitational effect can be varied through the widest range, by the use of mechanically created centrifugal force; consequently increasing this effect provides the most efficient means of hastening the separation of oil and water mixtures.

In figure 46 is shown the relationship between a settling-tank system and a centrifugal separator. In the former, the oil and water mixture enters the tank through a spout or compartment so that the mixture is led to the bottom of the tank with the minimum of disturbance to the contents. A partition running almost to the bottom of the tank allows only the heavier constituent (water) into the third compartment. The overflow for the water is slightly below that of the lighter oil, and, if separation is quick, continuous streams of pure oil and oil-free
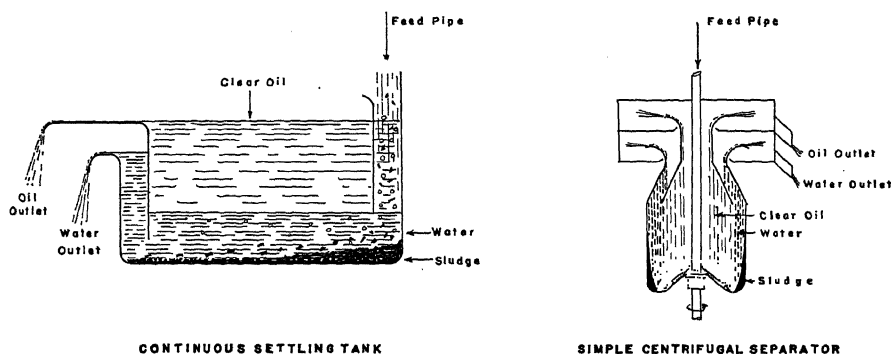
FIGURE 46. Settling tank and centrifugal separator.

water are obtained. The centrifugal separator operates in essentially the same manner except that the separation is along a horizontal plane. The effect of ordinary gravity in the vertical plane is almost imperceptible compared with the centrifugal force developed and the surface of the liquid is nearly parallel with the axis of rotation.

Centrifugal effect is usually represented by the force exerted on a mass of 1 lb. at the periphery of the centrifugal bowl. The equation usually given is $C = \dfrac{DN^2}{5866}$, where $D =$ diameter of bowl in feet, $N =$ revolution of bowl per minute, and $C =$ centrifugal effect in pounds exerted by 1 lb. at the periphery. The relationship between the centrifugal effect and linear velocity V is given by the equation $C = \dfrac{V^2}{57888D}$.

The centrifugal effect is therefore proportional to the square of the number

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of revolutions per unit time, and directly proportional to the diameter of the basket. In designs of centrifuges now available, some sacrifice bowl diameter in favour of high speeds, whilst in others a bowl of fairly large diameter but of medium speed is used. The type of bowl chosen for breaking oil-in-water emulsions depends upon a number of factors other than the actual centrifugal force developed. These factors are briefly touched on in the following paragraphs.

(ii) TYPICAL FEATURES OF SOME COMMERCIAL CENTRIFUGES

Typical of the small diameter, high speed centrifuges is the Sharples Super-centrifuge, a cut of which is shown in figure 47. The essential feature of this machine is the long tubular bowl
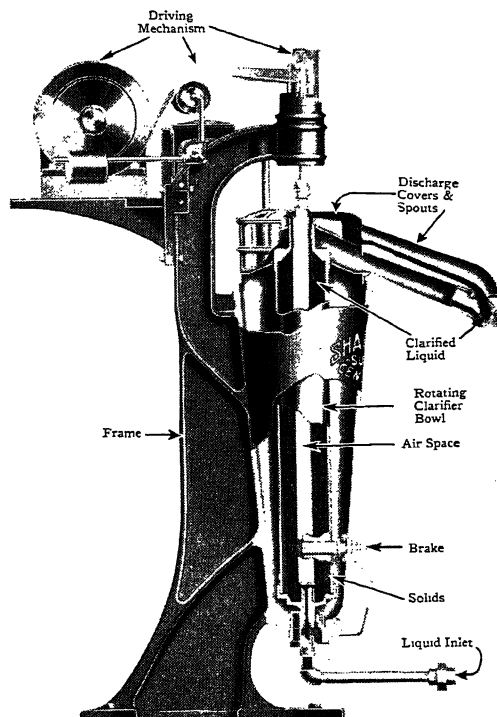
FIGURE 47. Cross-section, tubular clarifier bowl (Courtesy Sharples Specialty Co.)

fitted with removable rings for the variation of the discharge weirs. The bowl rotates at speeds ranging from 12,000 to 18,000 r.p.m. and it may be easily removed from the machine and quickly cleaned. The bowl is fed from the bottom and the entering jet meets a 3-wing baffle which quickly brings the liquor up to speed. In operation, the solids are thrown to the side of the bowl, building up a layer progressively thinner towards the top. The centre of the bowl is occupied by an air column, surrounded by the layer of oil, and finally the water. A separating ring, the diameter of which depends upon the proportion of oil and water, is attached to the top of the bowl and allows only the oil to rise through the inner outlet weir.

The actual separating area of this type of bowl is much smaller than in the disc-type bowls to be described later, but this is compensated for, in part, by the

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longer time the material is subjected to the centrifugal force and particularly by the high centrifugal force developed at the high speeds used. In the standard-size machine the bowl is $4\frac{1}{2}$ inches in diameter and 3 feet long, and, running at 17,000 r.p.m., the centrifugal effect developed is approximately 16,900 times that of gravity. The sludge-holding capacity of this type of machine is very small but on the other hand the easy removal and cleaning of the bowl is of undoubted advantage.

The Titan Company of Denmark and the Sharples Specialty Company of America have developed a disc-type of centrifuge that is capable of automatically removing any solid material deposited in the bowl. These machines, the Rotojector and the Superjector, are so designed that the deposits in the bowl are ejected at intervals through peripheral slots which can be opened or closed without stopping the machine. The essential parts of these machines are shown in figures 48 and 49. The bowl contains a number of discs AB where the actual separation of the
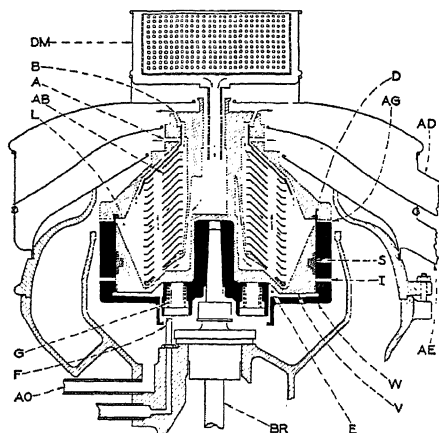
FIGURE 48. Roto- and Superjector in normal running position (Courtesy The Sharples Specialty Co.).
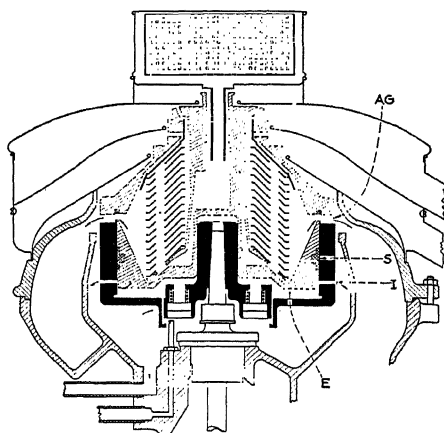
FIGURE 49. Roto- and Superjector in discharge position (Courtesy The Sharples Specialty Co.).

various constituents takes place. The operation of the Rotojectors and Superjectors is as follows: When used to separate two liquids such as oil and water, the mixture is fed through the funnel DM where it passes downwards to the bottom of the bowl. It then passes outwards and upwards through the separating discs AB. The oil moves to the inside of the bowl and is taken off at B and discharged through the spout AD. The heavy liquid moves outward and is taken off at A through the spout AE. Solids collect in the space L and are periodically discharged. For clarifying oils of solid particles, the heavy liquid discharge A is blocked off so that all the liquid has to pass out through the discharge B.

To discharge the machine without stopping, the inner bowl V, in which the solids accumulate, is made to slide in an outer bowl W to uncover an annular discharge slot AG, through which the solids are discharged. The inner and outer bowls are held together by springs G. The bowl is opened by introducing a small amount of water through the water inlet F into the chamber E. Hydrostatic pressure is generated in this chamber by the rotation of the bowl, and this forces the whole of the inner bowl to slide upwards, thus uncovering the discharge ports AG. When the unloading feed water is turned off, the water remaining in the pressure chamber E escapes at I,

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releasing the pressure and allowing the springs *G* to bring the bowls together again. The whole of the discharge operation can be controlled automatically.

The Rotojector and Superjector differ only in capacity; the former is rated at $3\frac{1}{4}$ tons and the latter at $6\frac{1}{2}$ tons of press liquor per hour.

A similar type of intermittently self-cleaning centrifugal separator is the Westphalia machine. The chief difference between this machine and the Rotojector is in the mechanism of opening the sludge-discharge ports. In this case water is allowed to flow through channels in the outer part of the rotating bowl. The pressure so developed operates a simple mechanism that opens the ports in the bowl and the solids are discharged. The opening and closing of the sludge discharge ports can be done automatically by means of a time clock. Working on pilchard "stick-water", one of these machines, set by time clock to dump every 10 minutes, was found to require 2 minutes to clear. At this rate the machine dumped out 24 gallons of wet solids per hour from 1500 gallons of "stick-water". Where no solids had to be dumped the capacity was 1800 gallons per hour.
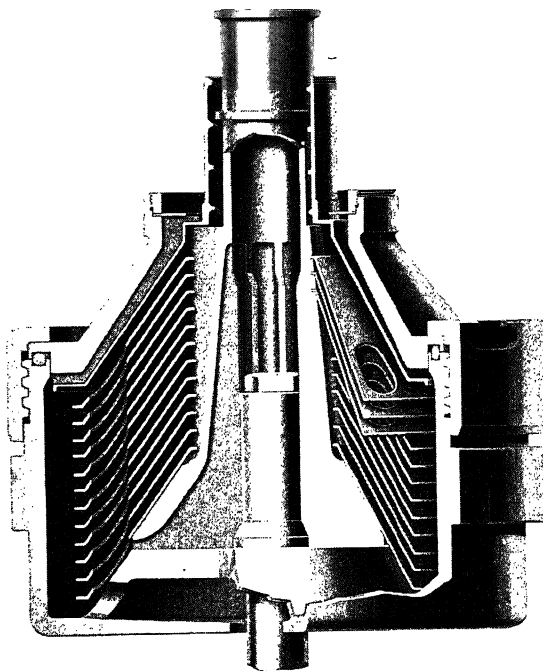
FIGURE 50. Purifier bowl—disc type (Courtesy De Laval Separator Co.).

The disc-type of centrifugal separator has been developed in America largely by the DeLaval Company who make two types of machines for the fish oil industry, an oil purifier and a continuously self-sludging separator. The disc separator, originally invented in 1890 by Dr. DeLaval, greatly increases the separating capacity of the bowl by reason of the increased surface area in which separation takes place. The separation takes place between the discs and therefore the distance an oil particle has to travel through the water phase is limited to the distance between the discs, i.e. about 1/20 of an inch. The discs are about 4 inches long and therefore the distance traversed by the oil particle in passing between 2 discs is about 80 times that of the thickness of the film. Another feature of the disc-type separators is the reduction in turbulence which can

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occur only during the time the mixture takes to reach the discs. Finally, since the larger part of the sediment accumulates in the outer part of the bowl, the building up of the solid cake is without effect on the capacity of the separating discs. This, of course, presupposes that all sediment is washed out of the discs by the outward-flowing aqueous liquor, a condition that obtains only in part. The construction and operation of a disc-type separator is shown in figure 50. The mixture enters the strainer at the top of the machine and passes through the tubular shaft to the bottom of the bowl, where it is distributed through small passages to the holes punched near the outer edges of the discs. It is desirable that the zone of maximum separation be in line with the holes in the discs, as this reduces the turbulence from excessive counter currents between the discs themselves. This zone of maximum separation is controlled by the use of discharge rings of various sizes acting against the water discharge, so as to balance the columns of water and oil
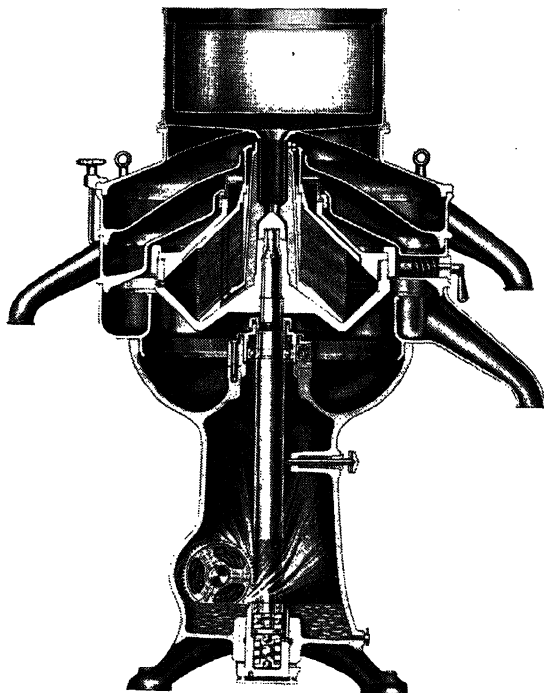
FIGURE 51. Cross-section view of De Laval SVKM-5 (Courtesy De Laval Separator Co.).

in the bowl. The size of discharge ring will therefore depend largely upon the amount of oil in the mixture. Final purification of the oil takes place between the discs, and the oil, owing to its lower specific gravity, travels inwards against the lower side of the upper disc, the water being forced outward along the upper side of the lower disc.

The DeLaval fish-oil separator (SVK type) shown in section in figure 51 differs from the purifier type chiefly in the design of the bowl. This is fitted, as usual, with a set of separating discs and a top disc with a neck through which the oil is discharged. There are, however, two outlets for the heavier components, one through the usual channels in the top disc and the other through a series of interchangeable nozzles screwed into the bowl wall. The heavy solids, together with some water, are forced through these nozzles and are thrown out into the bottom cover.

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Since the bowl must be kept full for efficient operation, the nozzles must be as small as possible and usually have a diameter of from 0.9 to 1.5 mm. Obviously, the particles in the liquor being treated must be smaller than this, and an efficient strainer must be used to prevent clogging of the nozzles. Working on screened herring "stick-water", and using a 1.2 mm. nozzle with a 140 mm. discharge ring, this type of machine will handle about 1500 gallons per hour. In the presence of 2.5 per cent dissolved protein and 1.5 per cent solid meal, the oil content of this herring effluent was reduced from 3 per cent to about 1.2 per cent. Analyses showed that the oil remaining in the centrifuged "stick-water" was largely associated with the finely-divided meal.

(iii) OIL-SEPARATING SYSTEMS USING CENTRIFUGES

The centrifuges just described can be used to separate the oil from the press liquors without the use of settling tanks or, as is more common, they can be used in conjunction with settling tanks to increase the yield of oil. In all cases, the
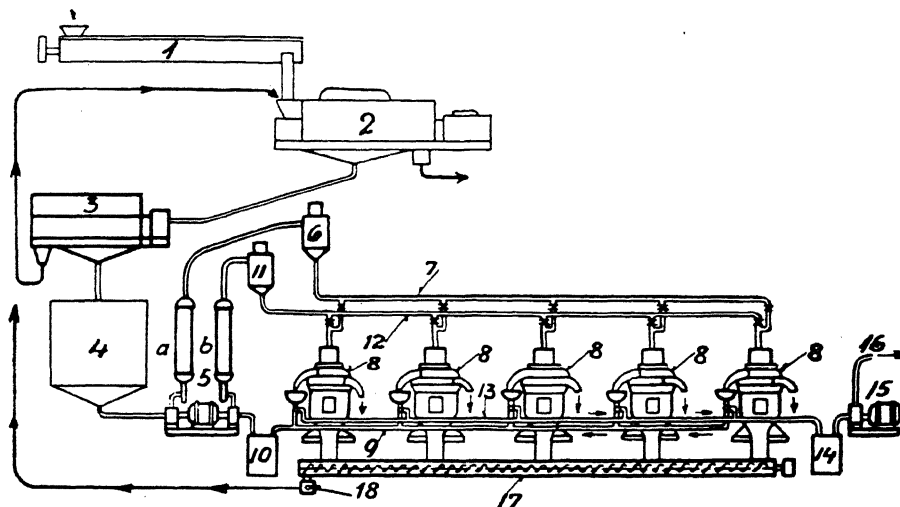
FIGURE 52. Centrifugal system in herring oil plant (Courtesy Titan Co., Copenhagen).

mixture going to the centrifuges should be free from large pieces of solid matter that tend to plug the centrifuge, and in addition the mixture should be pre-heated to a temperature between 180 and 200°F. There are various ways in which sludging and purifying centrifuges may be utilized, and the following descriptions illustrate only a few of them.

A centrifugal system installed by the Titan company in a Norwegian herring oil plant is shown in figure 52. This system entirely eliminates settling tanks. 1 and 2 are the cookers and presses. The liquor from the presses passes through a rotary screen 3 and from there to a single tank 4. From this tank the liquor is pumped through a "contact emulsifier" 5a. This contact emulsifier is set directly above the pump and consists of a large pipe into which steam is injected tangentially. The liquor is thus raised to the proper temperature for centrifuging and, owing to the strong swirling action, the emulsion is partly broken. The liquor then passes to a small surge tank 6, where it is distributed to three or four of the five Roto- or Superjectors 8. The recovered oil flows to tank 10 where it is pumped through a second contact emulsifier 5b, and

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from there through the fifth Roto- or Superjector, which removes the last traces of moisture and solid impurities from the oil.·

In the place of the surge tank 4 a settling tank can be used, in which case the recovered oil goes through a contact emulsifier directly to the final purifying centrifuge. The "stick-water" is treated as above. This plant is designed to handle 30 tons of press liquor from 40 tons of herring per hour.

Plants similar to this have been installed in Norway by the DeLaval Company, using SVK separators and oil purifiers. The press liquors are usually given preliminary separation in a settling tank and the "stick-waters" passed to a battery of SVK separators. These are fed through a surge tank directly heated with open steam. The oil from the separators and from the settling tanks is heated in a small surge tank before passing to the oil-purifying centrifuge.

Although many plants on the Pacific coast have installed centrifuges with complete elimination of settling tanks, the tendency seems to be towards combinations of settling tanks *and* centrifuges. Usually one or two such tanks are used and the oil is only partially separated, the remainder being recovered by the centrifugal separators. In all cases the liquor is passed through strainers before entering the centrifuge. Some of these settling tanks are arranged with baffles so that steam enters counter-current to the flow of the liquor from the first to the second tank. The separated oil goes directly to an oil purifier and the emulsion to the sludging centrifuges. One modern plant working on fresh salmon offal with a capacity of 5 tons of material per hour, has been able to get a complete separation and purification of the oil in a single passage through a centrifugal separator. The liquors from the press are pumped to a steam-heated surge tank equipped with removable strainers. They are brought to a temperature of about 200°F. and then passed through the centrifuge. The clear oil goes directly to storage and the discharge water is dumped.

As far as British Columbia is concerned, the use of centrifuges in fish oil plants is still quite limited. A few years ago installations were made of machines that were primarily designed as oil purifiers. The preliminary treatment of the press liquor was not adequate for the successful operation of these machines and their use was abandoned. Recently, however, some experience has been obtained with a separator of the new type. Working in conjunction with a settling-tank system and a strainer-equipped steam-heated surge tank, such a machine proved satisfactory when operating on herring "stick-water".

A word of caution may be of value here. Experience has shown that a centrifuge rarely functions perfectly the first time it is tried out. Such a machine is a precise piece of equipment and requires intelligent operation. When adjusted with suitable water-rings, and, in the case of the DeLaval machines, with suitable nozzles, so that satisfactory separation is being obtained, every effort should be made to keep the flow of "stick-water" to the machine constant in rate, composition and temperature. For any particular adjustment of a machine the allowable variation in composition of the raw material is strictly limited, and a great deal of the difficulty in the adoption of these machines to fish oil plants in the past can be ascribed to failure of operators to recognize this important fact.

Finally, since the character of press liquors varies enormously with (1) difference in the kind of fish, (2) locality in which the fish are caught, (3) season of

the year, and (4) method of processing, no manufacturer of centrifugal equipment is in a position to state definitely how this equipment will function when operating on all types of "stick-water". This should be taken into consideration when purchasing centrifugal equipment.

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SECTION 8. REFINING AND PROCESSING OF MARINE ANIMAL OILS

In this Section refining and processing have been differentiated since, in refining, the general chemical nature of the oil is not altered, only impurities or certain fractions of the oil being removed, but in processing, chemical transformations usually take place during which the original properties of the oil become changed. Standard methods for the refining and processing of fats and oils are, for the most part, applicable to marine animal oils. Owing to the highly unsaturated character of the latter substances, however, not all of the standard methods are suitable without modifications and these modifications have been indicated. Sufficient details of methods have been given to show the general nature of the processes.

I. REFINING

(*a*) REMOVAL OF FREE FATTY ACIDS.

Free fatty acids in vegetable and animal oils may be removed in a variety of ways, but in commercial practice refining with caustic soda is most generally used. Certain other methods such as esterification of the free fatty acids, and removal with solvents or by steam distillation have advantages in particular circumstances and will be briefly described.

(i) ALKALI-REFINING

This can be carried out in either a batch or a continuous process and consists simply in adding to the oil sufficient aqueous alkali to combine with all the free fatty acids present. The soap formed has certain adsorbent properties, given in detail later, and usually carries down with it a certain amount of colouring matter, finely dispersed tissue material, etc., and a proportion of the neutral oil itself. Some decolorization is therefore effected by this treatment. A typical alkali-refining plant is shown in figure 53. A charge of oil is pumped to the refining tank, which is equipped with suitable variable-speed agitators. The caustic soda solution is pumped from the dissolving tank to the measuring tank and sufficient of the solution run into the oil to neutralize the free fatty acids present. The strength of the caustic soda solution should be between 16° and 24° Bé (12 to 18 per cent), although, with oils containing more than 10 per cent of free fatty acids, stronger solutions are used. Usually a small excess (1 to 5 per cent) of alkali over that required for exact neutralization of the free fatty acids is added, particularly if the oil to be refined is very dark. The temperature and mode of addition of the alkali vary with the nature of the oil being treated.

As a rule, the oil is heated by means of closed steam coils to a temperature of about 24°C. (75°F.) and maintained at that temperature during the slow addition of the alkali. Stirring must be efficient but not rapid enough to produce

persistent emulsions. After complete addition of the alkali, stirring is discontinued and the temperature raised to about 46°C. (120°F.) until the soap settles out and the oil breaks clear with flocculent black specks in it. To facilitate the clear breaking of the soap, sodium silicate may be added along with the caustic soda, or salt may be added to "salt out" the sodium soaps. After thorough settling the foots are removed and the oil thoroughly washed, first with a salt solution and then with hot water.

In order to reduce the amount of neutral oil in the soaps and to avoid the formation of slow-breaking emulsions, due regard should be given to concentration of the caustic soda, temperature of the oil and rapidity of stirring. These three factors vary with different types of oils, but with fish oils it can be stated that in general low temperatures and fairly high concentrations of alkali may be
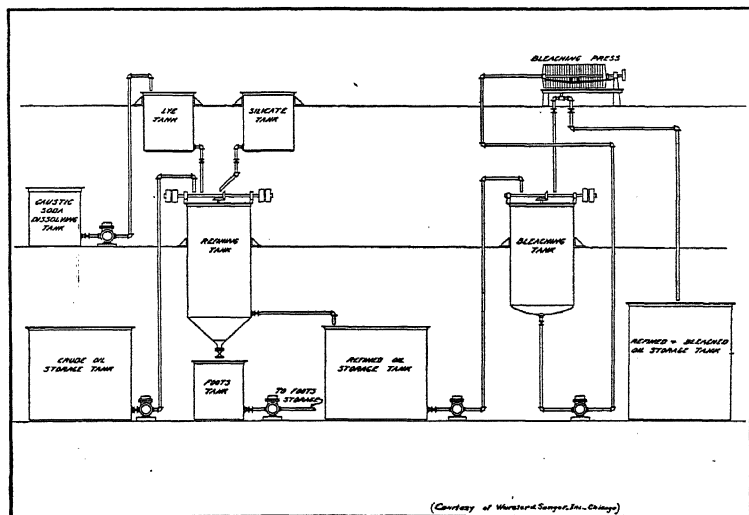
FIGURE 53. Alkali-refining plant.

employed together with slow stirring. The desirable conditions are such that, as the neutral point is reached, the soap will grain out and contain all the water in the mixture. In the grained condition the oil adsorption is at a minimum.

Sodium bicarbonate is frequently employed for alkali-refining purposes. The amount of decolorization of the oil is less than with caustic soda, but usually a higher yield of neutral oil is obtained. The soda ash solution should be heated to boiling and the oil at 80°C. (176°F.) added to the slowly stirred solution. The mixture may be heated with either open or closed steam coils. In the former case any tendency for the sodium soaps to emulsify is overcome by the addition of sodium chloride whilst in the latter case heating is continued until the moisture content of the soap decreases sufficiently to make the latter rise to the top of the oil. The second method gives larger yields of neutral oil.

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Slaked lime is a cheap and satisfactory material to use for neutralization purposes, but it does not colorize well. The lime is usually added in the form of a thick cream and the mixture heated with closed steam coils so that the greater part of the water is removed. When sufficiently dehydrated, the calcium soaps can be removed by filtration.
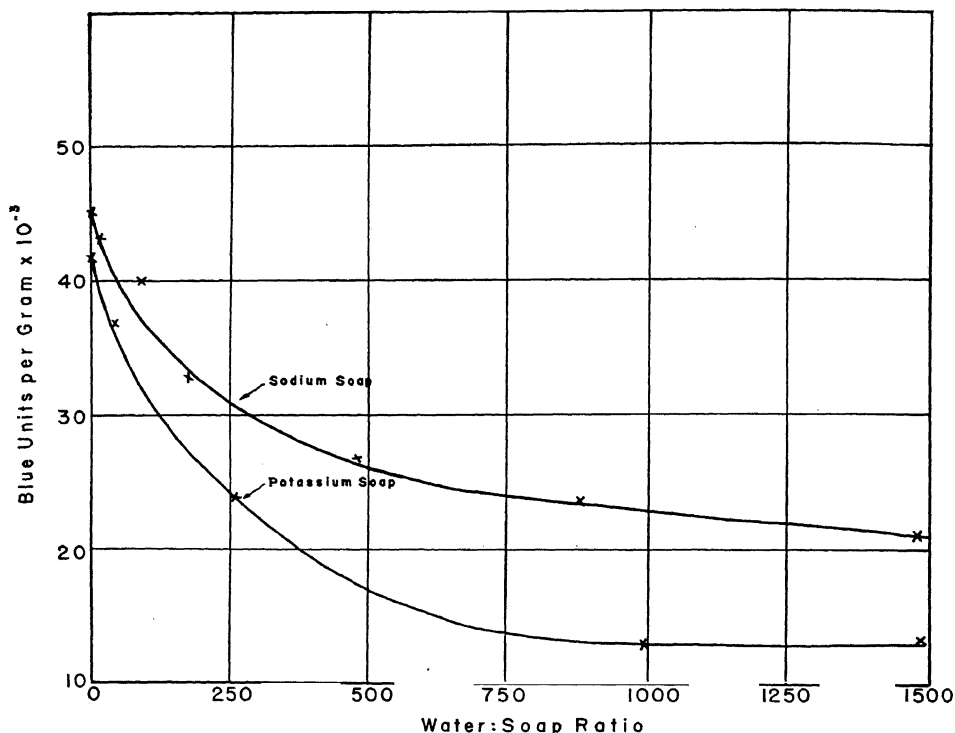
FIGURE 54. Effect of water-soap ratio on adsorption of vitamin A.

The washing of the alkali-refined oil with hot water does not necessarily remove all colloidally dispersed soap and several methods have been introduced to remove the last traces of such material. In addition to the use of centrifuges, filtering unwashed oil through filter presses containing special filter paper has been found to be successful, particularly when filter aids such as asbestos fibre or diatomaceous earth are used. It is essential that the latter be dry and added in sufficient amount to absorb the moisture associated with the colloidally dispersed soap.

The Sharples Specialty Co. has devised a continuous centrifugal method of alkali-refining, in which the flow of alkali and oil is automatically adjusted by a "proportionometer". The two liquids are intimately mixed in a specially designed mechanical mixer and then flash-heated to about 130°F. From the heater

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the mixture passes directly to a super-centrifuge of high speed, where the oil is rapidly separated from the soap sludge. The refined oil still contains traces of alkaline moisture and this is removed by continuous introduction of about 10 per cent of hot water, flash-heating to 165°F. and re-centrifuging. The finished oil then contains approximately 0.01 per cent of moisture and soap.
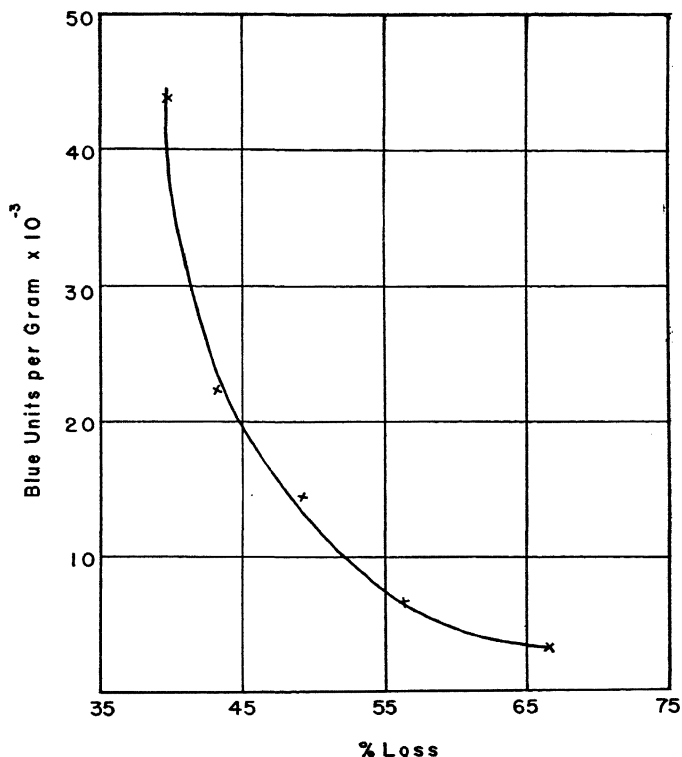
FIGURE 55. Variation of vitamin A removal with amount originally present.

Before leaving the subject of the alkali-refining of oil, attention must be drawn to the great adsorptive capacity of soaps formed *in situ* in oils. The decolorizing effect of alkali-refining is of course due to the adsorption of the oil pigments by the soap, but it is doubtful whether the full significance of this adsorptive capacity is appreciated, particularly in regard to the alkali-refining of oils containing vitamin A. The following data are taken from a paper by Brocklesby and Kuchel (1938), who investigated the adsorption of vitamin A from oils by soaps formed *in situ*. The most important single factor was found to be the water-soap ratio, the adsorption increasing with increase of this ratio up to the values of 3000 as shown in figure 54. The amount of adsorption, at equal water-soap ratios, was inversely proportional to the temperature between 40° and 70°C. and directly proportional to the free-fatty-acid content of the oil, i.e. the amount of soap formed. As shown in figure 55, the removal of vitamin A by adsorption varies with the amount of vitamin A originally present in the oil; the smaller the amount of the vitamin the greater is the proportional loss under otherwise identical conditions.

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It is only those soaps actually formed *in situ* in the oil that show these high adsorptive capacities. Preformed soaps added to a vitamin A oil only adsorb about one-sixth of the amount of vitamin adsorbed by the same soap formed *in situ*. Nascent soap has long been recognized as possessing a very active surface and this appears to be the explanation of the decolorizing effect of alkali-refining.

The adsorbed material, pigment or vitamin A, cannot be removed easily without first destroying the colloidal properties of the soap; solvents such as ethyl ether, petroleum spirits, etc., are practically without effect in removing the adsorbed material. Passage of the soap solution through high speed centrifuges and ultra-filters yields solutions optically blank as far as the presence of oil particles is concerned, but pigments and vitamin A are still retained. It thus appears probable that the pigments and vitamin A are preferentially adsorbed and due regard to this phenomenon should be taken when treating oils containing vitamin A with alkaline solutions.

(ii) STEAM DISTILLATION

This is not usually employed exclusively for the removal of free fatty acids, but when used for deodorization some removal of free fatty acids is effected. By this method it is not possible to reduce the free-fatty-acid content much below an acid value of 0.5, and for edible oils or fats, alkali-refining is preferred. For industrial fish oils that have to be deodorized, however, some reduction in the free-fatty-acid content may be expected and in some cases the alkali-refining step may be eliminated. Methods and equipment for the vacuum-steam treatment of oils are dealt with in (*d*) of this Section (deodorization), but it must be emphasized once again that the modern trend in this process is towards higher vacuums and higher steam temperatures. The use of as high a vacuum as practicable is to be recommended in the steam treatment of highly unsaturated fish oils.

(iii) ESTERIFICATION AND SOLVENT EXTRACTION

These are possible methods for the removal of free fatty acids, but as yet little, if any, commercial application of these has been made as far as fish oils are concerned. The esterification method involves the interaction of an alcohol with the free fatty acids, the resulting esters being removed by vacuum distillation if methyl or ethyl alcohol is used, or left in the oil if the esterifying alcohol is glycerine. A novel method involves the heating of the oil with a fat containing glycerides of fatty acids of low molecular weight, such as coconut oil. Ester-interchange occurs and the liberated low-molecular-weight fatty acids are steam-distilled off.

Free fatty acids may also be removed from an oil by solvents that exert a preferential solvent effect on the fatty acids. Alcohol, dilute acetone and methyl formate have been used for this purpose, but so far the method has not been adopted commercially. The production of neutral oils by the Wilhelm solvent process depends upon the greater solubility in dilute acetone of free fatty acids than of the neutral oil. The method is described in Section 7 (production).

(b) COLD CLEARING

"Cold clearing" is a physical process whereby a fatty oil may be separated into solid and liquid components by cooling. An oil, sufficiently cooled, begins

to solidify in crystalline form, and further cooling increases the amount of solid material. The liquid component of this mixture is variously known as "cold-cleared", "refrigerated", "wintered", "pressed" or "demarginated" oil. The solid material is called "stearine" or "stearin", although these names are also applied to commercial fatty acids. In this Bulletin "stearine" refers only to the solid glycerides of a cooled oil.

The changes in properties of an oil on cooling are of industrial importance. For example, an oil that will solidify or cloud at moderately low temperatures is undesirable for medicinal purposes. An oil used in paints must be cold-cleared because of the adverse effect of stearine on its drying properties. Again, stearine, which is more saturated than the oil from which it was separated, is preferable for hydrogenation because of its lower hydrogen consumption. The characteristics of an oil on cooling, the degree of saturation of the liquid and solid components, the methods for efficiently producing a cold-cleared oil, and the setting up of standards and tests for such oils are of commercial interest and as such were considered worthy of investigation in these laboratories.

(i) COLD TESTS

Crystallization of stearine from an oil is a slow process, making it difficult to determine the lowest temperature at which the oil will remain clear. For this reason various methods for measuring the ability of an oil to remain clear at a specified temperature have been proposed. The Committee on Analysis of Commercial Fats and Oils of the American Chemical Society defines "cloud point" as the temperature at which an oil clouds on cooling rapidly from 130°C.

TABLE XXXV. A cold test of commercially wintered pilchard oils

Description of oil	Storage temp.		Condition after storage for		
	(°F.)	(°C.)	5½ hr.	10 hr.	22 hr.
Below 50° cold test...	50-51	10	Faintly cloudy	Bottle half filled with stearine	Cloudy throughout with stearine
" " " " ...	52-53	11	Clear	......	Clear
Below 40° cold test...	40-41	5	Clear	......	Bottle half filled with light flocculent stearine
" " " " ...	35	2	Clouded throughout	......	Opaque
Below 32° cold test...	32	0	Clouded with small crystals*	Cloudy	Opaque; flocculent stearine somewhat settled
" " " " ...	35	2	Clear	......	Bottle one third filled with stearine

*Observation at 15 minute intervals showed that crystals were first apparent in 4½ hours.

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(266°F.) with stirring. In the "cold test" of the Official Methods of the American Oil Chemists' Society "winter oil" is defined as one which will remain clear after being immersed in ice and water for five hours. A "chill test" has been proposed for sardine oil (Behr 1936), which is a modification of the standard "cold test" of the National Cottonseed Products Association. The oil is heated to 120°C. (248°F.), transferred to 4-ounce sample bottles after cooling to 50°C. (122°F.), corked and sealed with paraffin. When cooled to room temperature the bottles are buried in cracked ice and water. The ensuing time in hours required for clouding is the chill test.

The writer examined several commercially cold-cleared pilchard oils bearing the description "Below t°F. cold test (5½ hours)", where t is the temperature at which the manufacturer guaranteed the oil to remain clear for 5½ hours. A 200 g. sample of each oil was warmed to 160°F. (71°C.) for an hour and then maintained at a temperature corresponding to that named on the label. Each was examined periodically for stearine. The results given in table XXXV indicate the slowness with which crystallization takes place, as samples which were clear after standing for 5½ hours at the given temperature deposited stearine on longer standing.

A preliminary attempt to devise a rapid cold test has been made in these laboratories, based on the solubility of an oil in acetone. When such a solution is cooled sufficiently, stearine crystals form which are very readily separated by filtering or centrifuging. The effects of temperature and of the proportion of acetone used are shown in data obtained from pilchard oil by Brocklesby and O'Neill in these laboratories, given in table XXXVI. The writer found a yield of about 4 per cent stearine on cooling a solution of 25 g. of pilchard oil in 40 cc. acetone in ice and water for two hours, but on repetition the results were not closely reproduced. Stirring increased the amount of stearine and improved somewhat the reproducibility of the results. Because of the difference in density between the stearine and the solution, centrifuging caused a rapid and complete separation, but again with inconsistent yields.

TABLE XXXVI.   Effect of temperature and concentration on the stearine formed from a solution of pilchard oil in acetone

Acetone (%)	5	10	25
Stearine at 44.5°F. or 7°C. (%)	5.5	3.3	2.2
Stearine at 38.5°F. or 3.5°C. (%)	11.8	10.8	5.7
Stearine at 35°F. or 1.5°C. (%)	18.1	14.6	13.5

(ii) STEARINE CONTENT OF SOME COMMERCIAL OILS

It is of importance to know to what temperature an oil should be cooled to remove a given percentage of stearine. Work done in these laboratories would indicate that this is not readily foretold.

A series of experiments was carried out to determine stearine content for various oils at various temperatures. In each case the filtered oil was maintained at 140°F. (60°C.) for 4 hours in a water bath, after which duplicate 50 g. samples were weighed into bottles which were then stoppered and returned to the water bath. After cooling overnight, the bath was transferred to a cold room at the desired temperature and left for 24 hours. The oil was then filtered in the cold room through cloth in a Büchner funnel with the aid of a vacuum pump. The results are shown in table XXXVII.

These data bring out several points of interest. The stearine content of herring oil is seen to be high in comparison with that of other fish oils. The stearine content of the herring oil samples from North Central B.C. shows an increase during the season as the fish approaches its spawning period, and this increase corresponds with an increasing saturation of the samples. The reduction of stear-

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TABLE XXXVII. Stearine content of various oils at various temperatures

	(°F.)	37	39	48	58	60
Temperature	(°C.)				15	16
Source of oil						
Herring (1937)						
North Central B.C., early..............		solid			3.8	2.8
(iodine value 154.2)						
North Central B.C., midseason and late.		thick			4.8	
(iodine value 141.2)						
North Central B.C., late..............		solid			8.7	4.7
(iodine value 139.3)						
Central B.C., early...................		solid			2.3	1.4
" " late...................		thick			11.4	2.8
Commercial sample.................						6.8
Pilchard						
August, 1938.......				24.8		
September, 1938....				29.5		
Commercial sample.		23.0		17.0		
Sardine, 1.				32.2		
" 2.		42.4		29.4		
Halibut, liver.				0		
" head.				7.7		
Salmon (1937), Central B.C.		6.6				
Dogfish liver						
Dec. 2, 1936..			1.1			
July 6, 1937..			1.4			
July 27, 1937.			trace			
Cod liver						
1. Wentworth process.....		12.0		trace		
2. Steam process.........		16.7		1.3		
3. Commercial wintered...		0*				
4. Commercial unwintered.		15.0		7.0		
5. Commercial..........		8.7		0		
6. Commercial..........		14.6		0.6		
Porpoise blubber........................		8.3				
Ratfish liver.		trace				
No. 1 Whale.		15.0				

*Sample 3 of cod liver oil formed a trace of stearine at 14°F. (−10°C.).

ine content by cold clearing is evident on comparing samples 3 and 4 of cod liver oil, of which 3 was a "quality" medicinal oil and 4 was labelled "unwintered".

Cod liver oil samples 1 and 2 contrast two processes of extraction which are described in Section 7; the Wentworth process is carried out at room temperature.

(iii) EFFECT OF COOLING RATE ON THE STEARINE OF HERRING AND PILCHARD OILS

In a series of experiments to determine the relation of rate of cooling to stearine yield and crystal size, 200 g. samples of filtered, crude pilchard oil and dried, filtered, crude herring oil were heated in stoppered bottles to 160°F. (71°C.) in a water bath for an hour, and allowed to cool in the bath to 70°F. (21°C.). They were then transferred to a large water bath at 70°F. in a temperature controlled room, which was thereupon cooled at a fairly constant rate of 3°F. (1.7°C.) per day. The temperatures of the oil and air were automatically recorded and were maintained at a difference of 2° to 3°F. Bottles of oil were removed at intervals and, after
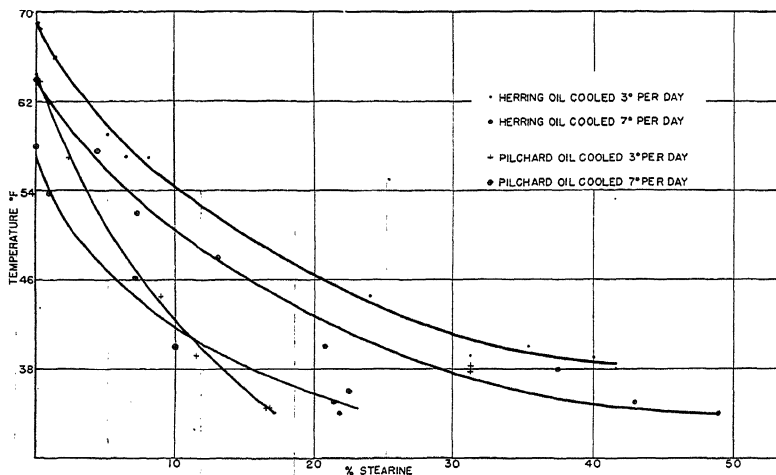
FIGURE 56. Effect of temperature on stearine content of pilchard and herring oils at two rates of cooling.

thorough mixing, photomicrographs through crossed nicols were made of drops from each. Each sample was then filtered through cloth in a Büchner funnel. The microscope and filtering system were in the same room as the water bath to prevent any change in the stearine crystals while being photographed and filtered. This experiment was repeated with a more rapid cooling rate of 7°F. (4°C.) per day. In both cases several of the cooled samples were left undisturbed for some time and were then examined as described above.

A somewhat similar experiment was carried out earlier by Brocklesby, Riddell and O'Neill at this Station and with pilchard oil from the same stock. In this experiment 200 g. samples of previously heated oil were placed in a water bath at 90°F. (32°C.), which was then allowed to cool in a room maintained at 41°F. (5°C.). The rate of cooling was therefore high at first and decreased steadily.

The yields of stearine for the two constant rates of cooling are shown in figure 56. The yield of stearine from herring oil at the faster rate of cooling was less at any given temperature than at the slower rate, which may be ascribed to the slowness of crystal formation. For pilchard oil, however, the two curves for the yields cross each other. At the slower rate of cooling the two final points in the herring oil curve and the two points rather remote from the pilchard oil

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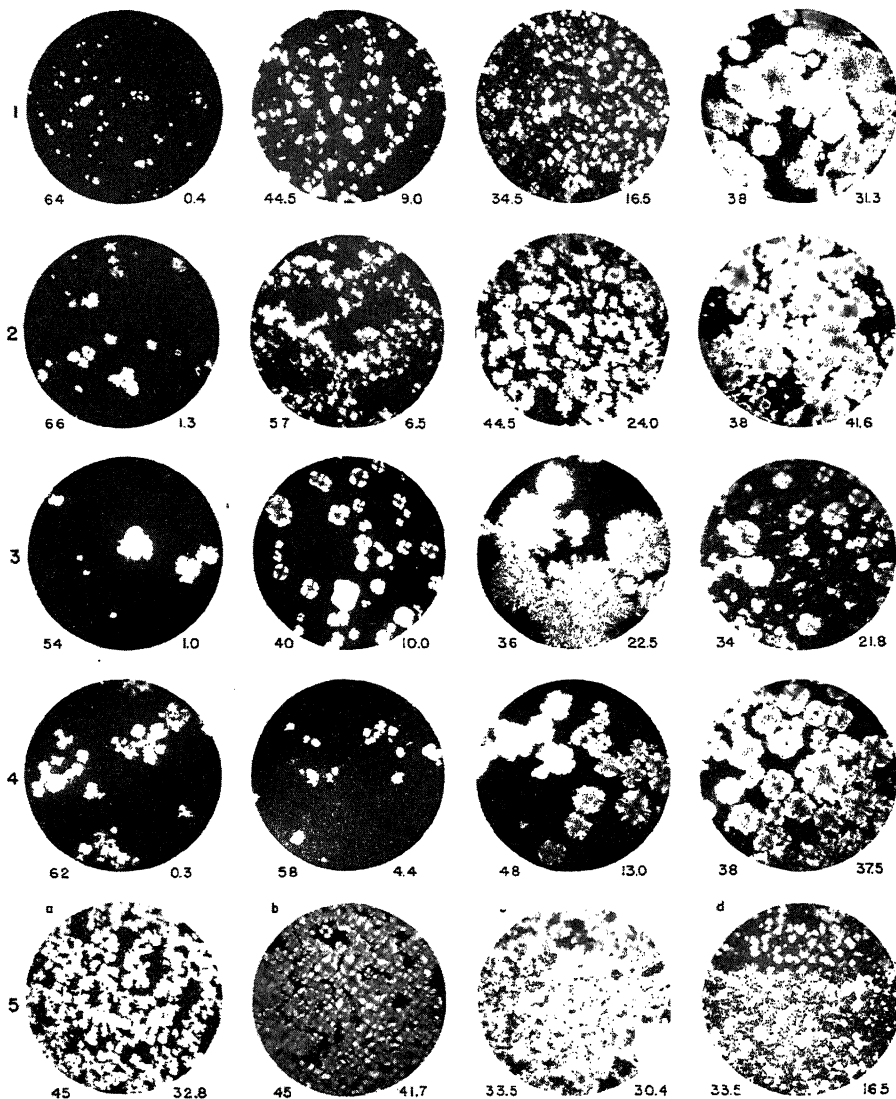
FIGURE 57. Stearine crystals of pilchard and herring oils between crossed nicols (×10). (Figure at left of photograph is temperature in °F.; figure at right is per cent stearine). (1) Pilchard oil, cooled 3°F. per day; (2) herring oil, cooled 3°F. per day; (3) pilchard oil, cooled 7°F. per day; (4) herring oil, cooled 7°F. per day; (5) (a) herring oil, cooled rapidly with stirring, (b) same without stirring, (c) pilchard oil, cooled 3°F. per day and vibrated, (d) same without movement.

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curve show the final yields after standing at 38°F. (3°C.) for two months. Thus three weeks, during which time the temperature was falling, was not sufficient time for crystallization to reach an equilibrium in either oil. However, at the faster rate of cooling the stearine yields at 34°F. (1°C.), obtained after standing three weeks at that temperature, showed an increase for herring oil but no change for pilchard oil.

In the experiment by Brocklesby, Riddell and O'Neill on pilchard oil, stearine appeared at 56°F. (13°C.) at a time when the oil was cooling at the rate of 16°F. (9°C.) per day. The stearine-temperature curve was linear, there being 19.3 per cent stearine at 41°F. (5°C.). After standing a week at this temperature the stearine content had increased to 27.8 per cent.

Other examples which show the dependence of stearine yield on conditions of cooling are the two values for "Pilchard oil, commercial sample" in table XXXVII, which were determined on samples from the same stock of oil as was used in the preceding experiments. Neither value lies on any of the three stearine-temperature curves for pilchard oils which have been described.

The photomicrographs taken in these experiments are shown in figure 57. At the slower rate of cooling (rows 1 and 2) they show that the increase in stearine content was due not so much to continuous growth in the size of individual crystals as to their increased number. The last picture of rows 1 and 2 shows, however, that on long standing (two months) there was a large increase in crystal size of some owing to the large increase in stearine during this time. Although the crystals separating from a saturated solution are normally increased in size by increased slowness of cooling, photomicrographs taken at the faster rate of cooling (rows 3 and 4) show a greatly increased crystal size as compared with those of the slower rate. These crystals, and the extremely large crystals in the third picture of row 3, which were seen in only one other sample, are considered to have been caused by some unknown and uncontrolled factor. The photomicrographs taken after 3-weeks' standing at 34°F. showed little change in the appearance of the crystals from previous ones in the same run, as is exemplified by the fourth picture of row 3.

(iv) FILTERING PROPERTIES OF HERRING AND PILCHARD OIL STEARINES

During the course of these experiments on cooling rates the time required for filtration was noted for each sample. At the slower rate of cooling the samples at the higher temperatures filtered in a matter of minutes while some at the lower temperatures required as long as two hours. The samples which had stood for two months at 38°F. (3.3°C.) and which contained the large crystals, filtered in less than a minute. At the faster rate of cooling all samples filtered within 4 minutes. These data indicate, as might be expected, that speed of filtration increases with crystal size.

It would therefore be highly desirable to be able to obtain large crystals at will. In the foregoing experiments two samples showed extremely large crystals, and in an effort to find a factor which might have caused them, the following experiment was carried out.

Test tubes of pilchard oil were cooled at various rates, always being held awhile at 80° to 100°C. (176° to 212°F.) before being allowed to cool. The samples included: (1) oil from the same stock as was used in the "3°F. per day" cooling experiment, and that had been stored in the interim at −20°C. (−4°F.), (2) oil from the same stock, but somewhat rancid from having stood for some time at room temperature, (3) the same as (2) but thoroughly dried with Drierite, and (4) the same as (2) but wetted by passing steam through it for one-half hour and keeping it at 100°C. (212°F.) until enough water separated for the oil to remain clear on cooling to room temperature. Macroscopic examination of the oils during any one rate of cooling showed no outstanding difference in crystal size among the samples. The yields of stearine measured by the depth of the crystals when settled in the test tubes were different, and varied considerably in amount from run to run, even when cooled at similar rates. Rates of cooling varying from

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1° to 40°F. (0.5° to 22°C.) per day produced crystals somewhat larger at the slower rates, but comparable on microscopic observation with the last picture in row 3 of figure 57. This would tend to show that "clean", filtered pilchard oil in the wet, dry or rancid condition behaves similarly over a considerable range of cooling rates.

The effect of stirring on the formation of stearine crystals was investigated. Duplicate 200 g. samples of herring oil from the same batch of oil as used in the "3°F. per day" cooling experiment were heated and allowed to cool in a bath of water originally at 127°F. (53°C.). One sample was stirred slowly; the other was allowed to stand undisturbed. The stirred sample showed the presence of stearine at 60°F. (16°C.), the unstirred sample at 57°F. (14°C.) After 13 hours the temperature had reached 45°F. (7°C.), and the samples were photographed (row 5 of figure 57) and filtered. The stirred sample required 50 minutes to filter and yielded 32.8 per cent stearine, while the unstirred sample required 2 minutes and yielded 41.7 per cent stearine. In this experiment stirring was detrimental both in time required for filtering and in yield of stearine, and the photomicrographs show that the unstirred sample contained better formed and slightly larger crystals.

Further observations on stirring were made, this time on pilchard oil. One of the samples in the "3°F. per day" cooling experiment was suspended in a position where a stirring motor
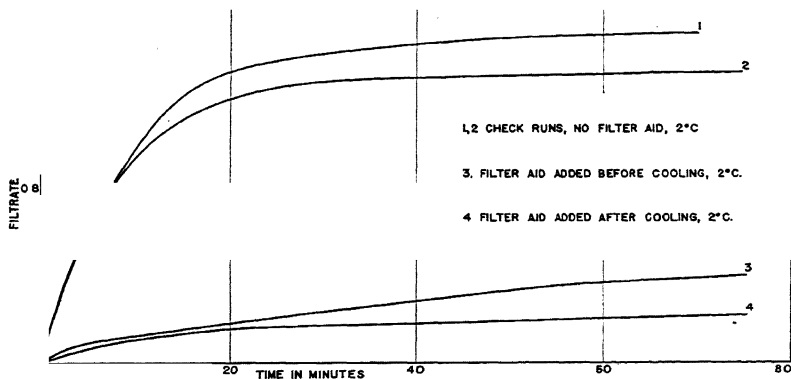
FIGURE 58. Effect of a filter-aid on the filtering properties of pilchard oil stearine.

kept it in continuous vibration. After 3 weeks of continuous cooling this sample and a comparable motionless sample were photographed and filtered at 34.5°F. The vibrated sample was full of stearine, required 120 minutes to filter, and yielded 30.4 per cent stearine. The unstirred sample was one-third filled with stearine, required 50 minutes to filter, and yielded 16.5 per cent stearine. As with herring oil the unstirred sample contained better formed and somewhat larger crystals (row 5 of figure 57), and filtered more rapidly. In both these experiments stirring impaired crystal formation and consequently increased filtration time.

An earlier experiment, in which 25 g. samples of pilchard oil were cooled for three hours in water at 9°C. (48°F.), showed a yield of 7.5 per cent stearine when the oil was quiescent and 10.5 per cent when stirred. These three experiments suggest the conclusion that stirring pilchard oil while cooling, either slowly or rapidly, increases its stearine content, but stirring herring oil, at least on rapid cooling, diminishes its stearine content. This conclusion is subject to modification when more data are available.

As "filter aids" are frequently used to speed filtration, the effect of their addition on the rate of filtration of stearine-containing pilchard oil was determined in these laboratories. In these experiments three-litre samples of filtered oil at room temperature were left in a cold room at the desired cold-clearing temperature for 24 hours. Each was then filtered in a small filter

press in the cold room using 10 lb. air pressure and a coarse canvas. In some cases 0.32 per cent by weight of a commercial filter aid was added to the oil before it was cooled, and in some cases the same quantity was added immediately prior to filtration. The volume of filtrate was noted at five minute intervals, and the volume-time curves are shown in figures 58 and 59.

It is clear from these curves that the rate of filtration of oil without filter aid decreased with lower temperatures, owing both to increased quantity of stearine, and to increasing viscosity of the oil. It is also clear that in these experiments the presence of a filter aid decreased the rate of filtration of the oil, particularly when added after stearine had separated. This may be due to the coarseness of the canvas used, since the filter aid, composed of particles far smaller than the stearine crystals, may have penetrated into the canvas, diminishing the size of its pores and therefore decreasing the filtration rate. A finer canvas might lead
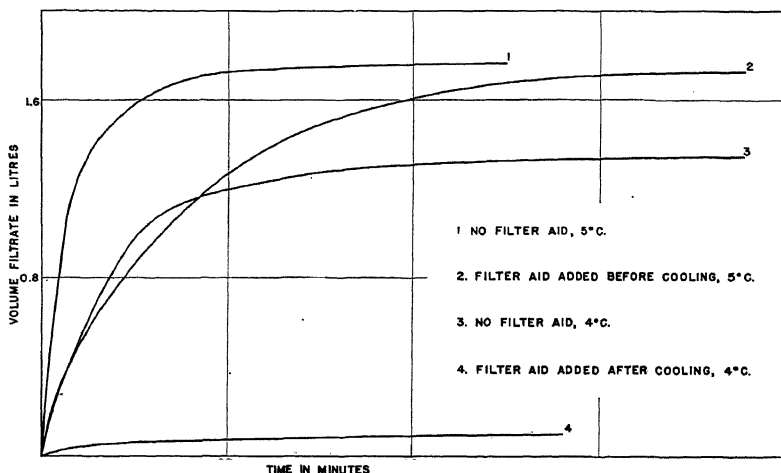
FIGURE 59. Effect of a filter aid on the filtering properties of pilchard oil stearine.

to different results. It is also possible that the pores between the particles of stearine were similarly reduced in size, reducing the filtration rate. It is conceivable that the addition of a "filter aid" of particle size comparable with that of the stearine crystals might lead to better filtration.

Still another factor is the high compressibility of a filter cake of stearine composed of soft particles. It is possible that the pressure used was too high, causing deformation of the crystals, with accompanying decrease in pore size. A lower pressure without filter aid would then lead to a longer period of filtration at the higher initial rate. Under these conditions the rate would decrease slowly as a result of the increasing thickness of the filter cake. A constant rate rather than a constant pressure of filtration, in which the pressure must be gradually increased from an initial small value to overcome increasing cake resistance, is a logical consequence of this hypothesis.

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It should be pointed out that when a filter aid is used to "polish" an oil by removing from it very small particles of impurities, a fine canvas is used, upon which the filter aid builds a coat to prevent the plugging of the pores in the canvas. In this case the filter aid increases the rate of filtration.

An attempt to filter a sample of herring oil repeatedly at successively lower temperatures to simplify filtration was unsuccessful. Filtration of a sample at 60°F. (16°C.), of the filtrate at 58°F. (15°C.) and of the second filtrate at 55°F. (13°C.) yielded a total of 18.7 per cent stearine with filtering time of more than 100 minutes, and finally produced an oil which was unfilterable at 50°F. (10°C.). A sample from the same stock of oil, cooled under the same conditions but filtered only at 50°F., required 40 minutes to filter, yielding 25.7 per cent stearine.

To determine the effect of pressing filtered stearine, a sample of herring oil stored at 47°F. (8°C.) for several days was filtered through canvas at a pressure of 7.7 lb. per sq. in. Twenty-four per cent of cleared oil was obtained with an iodine value of 126.5. The stearine was then pressed through the same canvas at 2000 lb. per sq. in., yielding a further 62 per cent of oil with an iodine value of 125.7. The residual 14 per cent of stearine had an iodine value of 94.1. These figures show that high pressure greatly increased the amount of cleared oil with but slight change in its unsaturation, and considerably increased the saturation of the stearine produced. They indicate further that stearine filtered with slight pressure is contaminated with a large amount of adhering liquid oil.

FIGURE 60. Stearine crystals from (a) crude pilchard oil, (b) alkali refined pilchard oil.

It is evident from the foregoing discussion that the formation of stearine in a condition suitable for its convenient removal is not a simple problem. While very rapid cooling to a low temperature produces a mixture which it is impossible to filter, the stearine obtained at the same temperature by slow cooling is more readily separable. The differences in the stearine crystals obtained at the two rates of cooling already described are felt to be due not to the different rates, for in qualitative experiments similar crystals were formed at rates of greater difference, nor to the presence of dissolved water, nor to the freshness of the oils, but to some unknown factor not under control. It is also clear that, notwithstanding their great utility in clarifying an oil, filter aids are not beneficial in the separation of stearine.

In all the experiments so far described crude oil was used. The effect of alkali-refining on the subsequent stearine separation has been investigated by Brocklesby and Denstedt (1933), and figure 60 is taken from their work. These photomicrographs, taken after identical cooling of crude and alkali-refined samples of pilchard oil, show that alkali-refining greatly increases the size and degree of perfection of the crystals formed. It is therefore preferable to precede cold clearing by alkali-refining.

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(v) EFFECT OF COLD CLEARING ON CHEMICAL PROPERTIES

The stearine content of a marine animal oil is related to its chemical composition. As described in Section 1, fish oils are triglycerides of fatty acids. These fatty acids are apparently distributed in random fashion throughout the molecules. They may vary from 5 to 26 carbon atoms in length and may contain from 0 to 6 unsaturated bonds. The melting point of a triglyceride rises with increasing number of carbon atoms in its fatty acids, but falls with an increasing number of unsaturated bonds. As an oil is slowly cooled, the triglyceride containing the greatest proportion of the longest and most saturated fatty acids will be the first to solidify. On further cooling, the last molecules to separate in solid form will be those containing the greatest proportion of short-chain and highly unsaturated fatty acids.

FIGURE 61.   Iodine value of stearine and cleared oil of pilchard and herring as increasing amounts of stearine are removed.

The iodine value of an oil is a measure of its unsaturation. It is therefore to be expected that the first stearine to separate will have a markedly lower iodine value than the original oil, while the cold-cleared oil will be but little changed because of the small amount of stearine removed. As the quantity of stearine increases, its iodine value will approach that of the original oil, while the iodine value of the cleared oil will increase. This is shown in figure 61 in which is given the iodine value of the stearines and of the cold-cleared oils of pilchard and herring separated at various temperatures.

That unsaturated fatty acids are contained in even the first stearine formed is shown by the fact that the initial stearine has a comparatively high iodine value. Correspondingly a considerable proportion of saturated fatty acids remains in cold-cleared oil as is shown by the experimental results given in table XXXVIII A, in which is given the per cent of saturated fatty acids remaining in

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pilchard oil as increasing amounts of stearine are removed. Behr (1936) reports a value of 16.77 per cent saturated fatty acids in a sample of sardine oil refrigerated to stand his suggested chill test for 90 to 100 hours.

TABLE XXXVIII

A. Saturated fatty acid content of pilchard oil cold-cleared at several temperatures

Temperature of cold clearing	(°F.)		46	40	34
	(°C.)		8	4.5	1
Stearine removed (%)...................		0	7.1	10.0	21.8
Saturated fatty acids in cleared oil (%).....		19.4	18.8	18.3	17.0

B. Saturated fatty acid content of cleared pilchard oil and stearine formed in acetone solution at several temperatures

Temperature of crystallization	(°F.)	28.5	23	14		−4
	(°C.)	−2	−5	−10	−15	−20
Yield of stearine (%)...................		10.2	14.9	16.0	21.7	34.3
Iodine value of cleared oil...............		190.6	190.8	195.4	197.5	205.6
Saturated fatty acids in cleared oil (%)....		17.2	16.3	15.2	14.3	13.2
Saturated fatty acids in stearine (%)......		39.6	36.6	35.3	34.5	30.2

A more complete removal of saturated fatty acids was obtained in these laboratories by Brocklesby, Riddell and Harding by the crystallization of stearine from an acetone solution of pilchard oil at low temperatures, the percentage of saturated fatty acids falling to 14.3 with 21.7 per cent of stearine removed. Their results, shown in table XXXVIII B also indicate the per cent of saturated fatty acids in the stearine. The trend of these data is of significance, although the total of saturated fatty acids in stearine and cleared oil is not constant, owing to the experimental errors both in the physical determination of stearine content and in the chemical determination of saturated fatty acids.

Pilchard oil dries because of its high unsaturation. The drying is more complete when stearine is removed from it as is shown by the following data, obtained by the writer in these laboratories:

Stearine removed (%)   0   1.0   7.1   10.0   21.4
Hardness (g.) ... 28.5±6.0   36.3±4.9   42.3±5.6   51.6±6.2   72.0±10.4

The oil samples, with varying amounts of stearine removed, were mixed with a cobalt drier and spread uniformly on metal plates. After 3 days the hardness of the films was measured with an apparatus developed by Denstedt and Brocklesby (1936), which measures the weight in grams necessary to force a rounded metal point through the oil film. Sixty values were determined for each oil. The high

probable error indicated after each value for hardness is presumably the result of cissing of the films, i.e. their failure to remain uniformly spread.   These errors reduce the statistical value of the measurements, but there is nevertheless a trend toward increased hardness of the film as increasing amounts of stearine are removed from the oil.   The difference between the hardness of the first and the last samples, 43.5 ± 12.0, is statistically valid.

In a sulphonated oil the amount of solid material separating decreases with increasing destearinization.

The effect of stearine removal on polymerization is described in Section 5, I.

(vi) INDUSTRIAL COLD CLEARING

In the removal of stearine from oil on a commercial scale two pieces of equipment are needed, a cooling tank and a device for separating the stearine. The oil may be cooled by several methods.   Brine may be circulated in pipes which are inside an insulated tank or which are against its outer surface.   Either method has the disadvantage of causing immediate solidification of the oil in contact with the cold surface, regardless of its melting point, with resultant loss of the more unsaturated oil.   It is preferable to circulate brine, the temperature of which is continually decreasing from the temperature of the liquid oil to the final low temperature desired, at a rate such that there is never a large difference in temperature between it and the oil.   Another arrangement is to have the tank in a cold room.   A slow and uniform cooling will then result because the heat loss of the oil is governed by heat transfer through the air.   The temperature of the cooling coils and the size of room and tank will govern the rate of cooling.

When the oil has been cooled sufficiently, it is transferred by pumping or by forcing with compressed air to a filter press which should be at the same temperature as the oil to prevent any loss in filtering ability of the stearine either by softening through warming or solidifying in the press through further cooling. The use of a centrifuge to remove the stearine is described in British patent 261,450.   The oil is agitated with steady cooling by brine, the latter constantly maintained $5°C$. ($9°F$.) below the temperature of the oil until the desired temperature is reached, when the mixture is centrifuged.   The impairment of crystal form by stirring is here not so important as in filtering.   However, more liquid oil may be held in the interstices of the poorer crystals, resulting in a less complete separation.

The differential solubility of the triglycerides of an oil in organic solvents has been suggested in several patents as a means of separating stearine.   German patent 656,132 describes the preparation of drying oils from stand oils of iodine value 95 to 110 by crystallization from 6 to 8 times the amount of a ketone, such as acetone.   U.S. patent 2,113,960 describes the cooling of a carbon disulphide solution to $-15°C$. to separate stearine.   British patent 402,651 (U.S. patent 1,974,542) describes the use of a normally gaseous hydrocarbon under pressure as solvent.   Cooling is accomplished by reduction of pressure and the resulting stearine is separated by filtration.

(vii) INHIBITION OF STEARINE FORMATION

Cold clearing is sometimes carried out solely to obtain an oil which will remain fluid at winter temperatures. In this case the stearine content represents a loss to the producer, and a means of preventing its deposition would be desirable.

U.S. patent 2,097,720 covers the addition of small amounts (0.1 to 0.5 per cent) of blown cacao butter to olive oil for this purpose. A sample so treated remained clear at least 4 years at 2° to 4°C. (35° to 39°F.), while a control sample became solid in a few hours (Clayton *et al.* 1937). The method failed with peanut and cottonseed oils. These workers have also found blown beef tallow to be effective, and blown cottonseed oil to be slightly so. They suggest that the stearine separates in colloidal rather than crystalline form because of the oxidized addendum, which adsorbs on the surface of the stearine molecule clusters and stabilizes them. In these laboratories neither blown cacao butter nor blown herring oil was found to modify stearine formation in herring oil.

The formation of stearine is delayed in pilchard oil by washing the oil under the proper conditions with dilute permanganate solution. Since permanganate is an oxidizing agent, it conceivably forms a product from the oil similar in stabilizing properties to the blown oils mentioned above. Herring oil separated from acid-treated reduction-plant press liquors also exhibits delayed stearine formation. It is possible that nitrogenous compounds are released by the acid from the protein in the liquors, and are adsorbed by the stearine molecules, preventing their precipitation.

An oil, alkali-refined in the cold, sometimes exhibits delayed stearine deposition. In this case the phenomenon appears to be due to the presence of colloidal micelles of acid soap which act as a stabilizer for the stearine by adsorption of the crystalline nuclei. The mode of action here is similar to that obtaining when preformed crystals of stearine are adsorbed by soaps formed *in situ* in the oil in the cold. An experiment was carried out to determine the extent of delay in stearine formation in herring oil by this treatment when applied at several temperatures. A litre of warm, clear herring oil was cooled at a rate not exceeding 8°F. (4.5°C.) per day. After thorough mixing, samples were withdrawn at 70°F. (21°C.), 60°F. (16°C.), 57°F. (14°C.) and 50°F. (10°C.). Each sample was divided and one portion was mixed with dilute sodium carbonate solution containing sufficient sodium chloride to grain out the soap produced. This mixture and the untreated portion were immediately and simultaneously centrifuged for one-half hour at 2,500 r.p.m. In each case the room and reagent temperatures were the same as that of the oil so as to prevent any change in the stearine on that account, although the temperature in the centrifuge did rise a few degrees owing to the heat of the motor.

The separation of stearine by centrifuging was incomplete in the control samples at the two lower temperatures. On the other hand, the alkali-treated samples always separated readily in the centrifuge, the mixture of soap and stearine forming a solid cake between the oil and water layers. The resulting oil contained a cloudiness which settled out with time as a flocculent precipitate. A portion of this oil was then heated an hour in boiling water, which increased the amount of precipitate in the 60° sample and removed it in the 50° sample.

The various samples obtained were cooled at the rate of 8°F. per day or slower, after preliminary warming to about 120°F. The temperatures at which stearine crystals first appeared are shown in table XXXIX. Only the sample alkali-treated at 50°F. showed delay in stearine formation, and in this case the control contained stearine, even though centrifuged for an extra period of 15 minutes.

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TABLE XXXIX. The effect of alkali-refining at several temperatures on stearine formation in herring oil

Temperature of alkali treatment and centrifuging (°F.)	70	60	57	50
Stearine removed (%)............................	0	5	37	47
Temperature of initial stearine formation (°F.)				
Control..................................	65	60	51	50
Alkali-treated............................	65	60	48	44
Alkali-treated, heated....................	65	60	51	44

Two incidental observations may be of interest. The alkali-treated samples, when cooled rapidly, became turbid, gel-like semi-solids, with no indication of particle formation. With slow cooling they showed a marked tendency to crystallize on the wall of the container, which was not observed in the control samples.

Treatment with magnesium and calcium hydroxides, alkaline sodium silicate and phosphoric acid followed by sodium hydroxide were all unsuccessful in delaying stearine formation.

U.S. patent 2,050,528 protects the addition of small amounts of lecithin to wintered cottonseed oil to prevent further crystallization of stearine. It is known that salmon egg oil, which is high in phosphatide content, is difficult to freeze. One sample was found to be fluid, though viscous and cloudy, at $-20°C.(-4°F.)$. Reference to table XXXVII shows salmon oil (containing some egg oil) to be low in stearine. It is possible, then, that lecithin and related compounds also act as protective agents for colloidal stearine. However, the addition to herring oil of three different commercial samples of lecithin, salmon egg oil, and the acetone insoluble fraction of salmon egg oil had little or no effect on stearine formation.

(c) DECOLORIZING

The colour of a marine animal oil is due to pigments occurring naturally or developing after the death of the animal. The natural pigments include carotene, xanthophyll, fucoxanthin, astacin and chlorophyll. Other pigments may result from spoilage of the animal before extraction of the oil, from cooking the animal, and from heating the oil after extraction. The properties of these pigments are more fully discussed elsewhere (Section 3). The intended use of an oil determines both the required degree and the method of decolorization. Methods may be classified as chemical or physical.

(i) CHEMICAL TREATMENT

This destroys the pigments by either reduction or oxidation reactions. Reducing chemicals include hydrogen and zinc dust. Oxidizing chemicals include oxygen, dichromates, chlorates, hypochlorites, hydrogen peroxide and organic peroxides. Chemicals must be used with discretion for they not only destroy the pigment but may also attack the oil itself. Ease of attack will increase with increasing unsaturation of the oil.

In the hydrogenation of an oil, its colour is almost immediately destroyed. The writer has found the colour of a sample of pilchard oil to change from brown

to light yellow in ten minutes of hydrogenation at 180°C. (356°F.) with 30 lb. pressure of hydrogen in the presence of 0.7 per cent nickel supported on kieselguhr. The iodine value simultaneously decreased from 177.9 to 111.1.

A German patent, 634,043, describes the combined deacidification and bleaching of an oil by mixing it at 150°C. (302°F.) or higher with powdered zinc.

Air (oxygen), used for decolorizing palm oil by oxidation, is of relatively little importance for fish oils, since it is a cause of rancidity, which is, of course, to be avoided.

Sodium and potassium dichromates are active oxidizing agents in the presence of an acid. For decolorizing palm oil, usually destined for soap making, 1 per cent of dichromate salt is dissolved in water and stirred into the oil warmed to 50°C. (122°F.), and 5 per cent concentrated hydrochloric acid is immediately added with stirring. After half an hour the mixture will have separated into two layers, and 25 per cent of boiling water is then sprayed over it. If in two hours the oil is still green in colour, it is boiled with 10 per cent more water and 0.1 per cent acid and again allowed to settle. Decolorizing is more effective with a succession of treatments followed by washing after each. Sodium chlorate is employed similarly, using 1 to 1.5 per cent of the salt and 5 to 10 per cent of 1:1 sulphuric acid.

British patent 444,813 (U.S. 2,022,738) describes the use of calcium or sodium hypochlorite in concentrated water solution added to tallows at 40°C. (104°F.) in small amounts. The mixture is acidified with hydrochloric or sulphuric acid.

Use of nascent chlorine resulting from electrolysis of sodium chloride solution is described in Belgian patent 375,716. The chlorine is subsequently eliminated by the sodium hydroxide simultaneously formed in the electrolysis. However, the product from such a treatment would be chlorinated as well as bleached.

Hydrogen peroxide is an important chemical for oil decolorization, since it decomposes into water and oxygen, leaving no other residue. The oil, heated to 40° to 80°C. (104° to 176°F.), is treated with 0.5 to 2.0 per cent of 30 or 45 per cent hydrogen peroxide, which is added in a thin stream to the stirred oil. Stirring is continued for 2 to 5 hours until the required decolorization is effected. A smaller amount of hydrogen peroxide is required if the oil is first acidified with 1 per cent of 70 per cent sulphuric acid. The simultaneous or successive addition of equal quantities of hydrogen peroxide and acetic anhydride is covered by German patent 632,516. Use of organic peroxides, as benzoyl peroxide or peroxides of fatty acids, is covered by U.S. patent 1,838,707. Austrian patent 109,719 describes the combined use of hydrogen peroxide and more or less insoluble peroxides, as that of barium. Two different patents, Austrian 137,324 and French 762,166, cover the use of any peroxide followed by an adsorbent.

Several recent patents by different inventors, including U.S. 2,122,260, U.S. 2,116,344, U.S. 2,110,789, U.S. 2,003,076 and Brit. 327,990, cover the bleaching of oils by heating to 230° to 280°C. (446° to 504°F.) in a vacuum. In two of these an inert gas is simultaneously passed through the oil. With the more unsaturated fish oils this treatment, if prolonged, would lead to polymerization [Section 5 I(d)].

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Chemical decolorizing of an oil must be carried out in a container which is not attacked by the chemical. Such containers include: wooden, earthenware, glass and porcelain vessels; vessels lined with lead, tin, vanadium steel, aluminium or stoneware plates; and enamelled, glass-coated or tin-coated iron vessels.

Some of the methods just described have been applied only to vegetable oils. The writer has tried several on samples of alkali-refined salmon and pilchard oils. The results are summarized in table XL. The colour of the oil, contained in a 13-mm. cell, was measured in Lovibond units of yellow and red. It should be mentioned that neither concentration, temperature, nor time of reaction was necessarily the optimum.

TABLE XL. Decolorization of pilchard and salmon oils with chemicals, measured by Lovibond units of yellow (Y) and red (R)

Treatment	Salmon		Pilchard	
	Y	R	Y	R
1. Original oil	29	5.0	15	1.3
2. Zinc dust and glacial acetic acid at 60-70°C. (140-158°F.) for 2 hours	11	2.3	9	1.0
3. Zinc dust at 60-70°C. for 3 hours	19	4.1	14	1.3
4. Glacial acetic acid at 60-70°C. for 3 hours	13	2.4	10	1.0
5. Zinc dust at 160-170°C. (320-338°F.) for 2½ hrs.	29	5.7	29	3.2
6. Oil at 160-170°C. for 2½ hours	30	7.3	30	5.2
7. 1.5% potassium dichromate and 5% conc. HCl at 50°C. (122°F.) for 2½ hours. (Readings approximate)	13	2.0	13	2.0
			8	1.4
8. Potassium chlorate solution and dilute H_2SO_4 at 60-70°C. for 1 hour	29	4.7	13	1.2
9. 1% of 30% H_2O_2 at 50°C. for 3 hours	18	4.4	8.7	0.9
	18	4.2	7.0	0.8
10. Above sample heated to 80°C. (176°F.) for 3 hours	6	1.0	2.3	0.1
			2.2	0.2
11. 1% of 30% H_2O_2 and 1% of 16% H_2SO_4 at 60-70°C. for 5 hours.	9	1.2	5	0.5
	9	1.2	5	0.4
12. 1% of 30% H_2O_2 at 60-70°C. for 5 hours. (Control with no. 11)	12	3.0	5.6	0.6

The greenish emulsion which is produced with potassium dichromate was very difficult to break in the case of pilchard oil, being resistant to centrifuging. Filtering with a filter aid cleared it fairly well. Of duplicate samples of salmon oil, the emulsion formed in one remained stable on filtering, while the other cleared to some extent. The use of 70 per cent sulphuric acid preceding hydrogen peroxide treatment caused an immediate blackening in both oils, which could not be removed by filtering. Sixteen per cent sulphuric acid, however, caused no discoloration. Of the methods tried, acidified hydrogen peroxide seemed to give the best results. The advantage of the presence of acid is shown by comparing experiments 11 and 12 in the table above. The effect of increased temperature and time is evident on comparing 9, 10 and 12. Comparison of 2, 3 and 4 shows

that glacial acetic acid, soluble in both oils, caused some decolorization and was almost as effective alone as when added with zinc.

(ii) PHYSICAL METHODS

Since these involve little or no chemical change in the oil, they are better adapted to fish oils than are chemical methods. Physical methods depend upon the phenomenon of adsorption whereby the pigments adhere tenaciously to the surface of an insoluble, finely-divided material, which is added to the oil under suitable conditions and removed by filtration. Activated carbons and natural or activated bleaching earths are commonly used, although some synthetic products have been patented.

Carbons are prepared from organic material by charring. Activated carbon is produced when certain chemicals, such as phosphoric acid, zinc chloride, or ferric chloride, are added to the material and removed by acid after the charring. Treatment of the carbon at high temperatures with a gas, as steam or chlorine, also results in activation. Various activated carbons are produced commercially.

When using carbon, 0.5 to 1 per cent is added to the heated oil and the mixture is agitated for 15 to 30 minutes. Removal of the carbon is effected by filtration. The first oil to come through contains some carbon and must be returned to the press for refiltering until a retentive cake has been built up on the filter cloth. A pre-coat may be formed by passing a bleached oil containing a filter aid through the press, followed without pause by the carbon-containing oil. The optimum quantity of carbon, time of contact and temperature vary with each oil and must be determined by experiment. The proportion required in the laboratory experiments is generally in excess of that required in the plant.

Various modifications of this method have been suggested. Several patents, including U.S. 1,856,571, Dutch 21,342 and German 532,211, describe the acidification of the carbon with 0.5 to 1 per cent of hydrochloric or sulphuric acid before adding it to the oil. It is claimed to be preferable to add the carbon in several small portions at 20-minute intervals. In the counter-current method, previously-used carbon is added to the oil, removing some of the colour. This is filtered off and fresh carbon is added to remove the remaining colour. In this way the full adsorbing capacity of the carbon may be utilized. Canadian patent 370,570 (U.S. 2,105,478) covers the simultaneous addition of sodium carbonate, carbon and water. The carbon and soap formed are filtered off together, producing a bleached, refined oil.

Carbon has a tendency to cause oxidation of the oil to which it is added. This is probably due to the increased activity of the oxygen which is adsorbed on the carbon. Maintenance of a vacuum over the oil that is being treated decreases this possibility.

Decolorizing earths, such as fuller's earth, bentonite and other naturally occurring clays, are widely used because they involve no chemical change. Some earths may be greatly improved in decolorizing ability by activation. U.S. patent 2,079,854 describes an increase of 10 per cent in activity of fuller's earth by extruding it when moist at a pressure of 500 lb. per sq. in. Digestion of an earth with a mineral acid, as hydrochloric or sulphuric, may increase its activity, and U.S. patents 1,819,496 and 1,980,569 cover a commercial product so prepared.

Similar activation of bentonites is covered by U.S. patents 1,776,990 and 1,929,113 and of other clays by U.S. patents 1,913,960 and 1,649,366.

Table XLI, taken from work done at these laboratories (Brocklesby and Moore 1933), shows the bleaching activity on pilchard oil of several British Columbia earths. In each case the oil was stirred with the optimum proportion of earth at the optimum temperature for 15 minutes and then filtered. The temperatures and proportions of earth are indicated in the table and represent the range in general use. The bentonite was activated by boiling with hydrochloric acid for 6 hours.

TABLE XLI. Decolorization of pilchard oil with British Columbia earths, measured by Lovibond units of yellow (Y) and red (R)

Type of earth	Amount used %	Optimum temperature		Colour removed (Duboscq) %	Colour remaining (Lovibond)	
		(°C.)	(°F.)		Y	R
Standard activated earth...........	3.0	65–85	149–185	88.6	1.5	0
Diatomite........................	5.0	90–92	194–198	79.8	2.3	0.1
Bentonite........................	7.0	90–92	194–198	80.2	3.1	0.2
Diatomite No. 2..................	5.0	70–80	158–176	80.2	1.9	0.1
Volcanic ash No. 2...............	7.0	90–125	194–257	75.0	2.7	0.2
Activated bentonite acid earth......	3.0	75	167	88.4	1.3	0
Activated bentonite washed neutral .	3.0	93	199	85.0	1.5	0

Table XLII shows the bleaching activity on pilchard oil of several Canadian bentonites. In each case the oil was stirred with the earth at 120°C. (248°F.) for 5 minutes. The earths were activitated by digestion with sulphuric acid, which dissolved out some alumina. Each earth required a different acid concentration and a different time of boiling for best results.

TABLE XLII. Decolorization of pilchard oil with bentonites (Gallay 1938), measured in yellow (Y) and red (R) units

Source of clay	Amount used (%)	Residual colour (Lovibond) R
California (activated).......................	2.2	0.0
California (activated).......................	1.4	0.0
Manitoba.................................	2.6	0.0
Manitoba.................................	1.3	0.0
Manitoba, activated........................	1.3	0.0
Manitoba, activated........................	0.4	0.0
British Columbia..........................	2.0	0.0
British Columbia, activated.................	1.1	0.0

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The addition of 1 to 10 per cent water to an earth has been frequently recommended to improve bleaching. It is claimed that the presence of soap or alkali in the oil reduces the efficiency of the earth, and that the presence of soap causes increase in free-fatty-acid content.

The use of earth and carbon alternately or together is recommended, at least for certain vegetable oils, in that a small amount of carbon greatly decreases the amount of earth required with no loss in bleaching power. This has the advantage of decreasing the loss of oil which is retained by the earth as well as decreasing the size of filters required and the amount of handling.

(d) DEODORIZATION

Formerly it was considered that the odour of fish oils was due to the presence of ammoniacal residues left in the oil during processing. Under the earlier system of oil production, where fish were allowed to rot, this was probably true, and the oils had an odour distinctly characteristic of protein decomposition products. With the modern processes it is rare to encounter this type of odour. The odour that develops in carefully prepared oils is due to the oxidized products of the highly unsaturated fatty acids of the oil that are very susceptible to oxidation.

While it is possible to remove these products by ordinary deodorization methods, the odour returns owing to further oxidation of these acids. The only method of permanently deodorizing such an oil is to hydrogenate it until the highly unsaturated acids are reduced to a lower level of unsaturation. ·

At present deodorization usually consists of passing superheated steam through the oil or fat at either normal or reduced pressure, during which process the decomposition products and any·free fatty acids are removed by distillation.

Modern methods tend toward increasing the working temperature of the oil and the superheated steam to as high as 250°C. (482°F.), decreasing the pressure and increasing the area of contact of the oils with steam. This is secured by spraying the oil into the deodorizer (Brit. pat. 285,380) or feeding the oil continuously over a perforated plate which is supplied with a steam blast (Brit. pat. 248,828). According to Andrews (1926) vacuums of less than half an inch of mercury and temperatures up to 200°C. (392°F.) and over are common. Regarding the method of producing the vacuum, this author prefers the barometric condenser with tail pipe discharge because the system is automatic, cannot easily choke up, is mechanically simple and uses but a small amount of cooling water. The theory of steam refining of saponifiable oils has been treated by Brash (1926) in two excellent articles. From the data given in these papers the relative dimensions of the apparatus and the form of the outlet pipe may be calculated. To shorten the time of deodorization the most important factors are low pressures in the deodorizer and high temperature of the oil.

Plants for the vacuum-steam treatment of oils are available for operation under medium or high vacuums. Equipment typical of the former plant consists of a deodorizer and a vacuum unit which includes a jet condenser mounted on a wet vacuum pump and cooling coil. With condensing water at 20°C. (68°F.), a

pressure of about 120 mm. is attainable in the deodorizer, and with steam at 100 lb. pressure a temperature of 170°C. (338°F.) can be reached. For high-vacuum work the vacuum unit consists of thermocompressor (which compresses the vapours from the deodorizer into the condenser), a barometric condenser and a two-stage steam-jet vacuum pump. With such a system pressures of about 12 mm. can be obtained in the deodorizer.

Continuous processes such as the Wecker in Germany, and the Tolman-Goranflo in the United States, while used mainly as fatty acid distillation processes, are also admirably suited to deodorization which is essentially a distillation process.

Numerous methods involving the use of other inert gases such as hydrogen, nitrogen, fuel gas, etc., have not shown any great advantage over the use of steam. Many methods have been suggested which make use of odour-masking substances, and methods have been advocated for washing out the odorous materials, using various solvents, or adsorbing them on suitable adsorbents. None of these has met with marked success.

Not only must the fish oils be deodorized, but before the hydrogenated products can be used in edible oil products, they must be deodorized to free them from the "catalyst" or "hydrogenation" odour. This odour is due mainly to alcohols formed during the process and is removed by steaming under reduced pressure.

The recently developed high-vacuum molecular or "short-path" distillation process can be applied to deodorization also. By subjecting the oils to the high vacuums obtainable by modern forms of apparatus, the odoriferous substances may be distilled using the methods and apparatus described in Section 8 II(*g*) (distillation).

II. PROCESSING

(*a*) SAPONIFICATION

The nature and course of hydrolytic and saponifying processes as applied to fats and waxes have been described in Section 5 I(*a*). Some technical aspects of these processes as applicable to the conversion of marine animal fats into fatty acids, soaps and glycerol are now presented. The hydrolysis and saponification of marine animal waxes to yield fatty acids and fatty alcohols are technically feasible processes, though requiring more drastic conditions than in the case of fats; recent progress in the commercial production of fatty alcohols from other sources [(Section 3 III(*d*)] has removed the necessity of relying on natural waxes as raw materials for such alcohols, and, except where some specific fatty acids of such waxes are desired, fatty acids are more readily obtainable from fats.

Hydrolysis is here considered as the splitting of fats to yield chiefly free fatty acids and glycerol, although admitting the presence of a catalyst which may combine with a small proportion of the fatty acids formed; the separated fatty acids may later be saponified in a separate process to form soaps. The term *saponification* is here employed to designate fat-splitting accompanied by essentially

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simultaneous soap formation between the alkali used in the saponification and all of the fatty acids produced; these soaps may represent the desired product (with or without the accompanying glycerol), or they may act as intermediate products for the later separation of free fatty acids and glycerol.

The principal fat-splitting processes used commercially are: *Hydrolytic*— (1) autoclaving with steam alone; (2) autoclaving with acids; (3) autoclaving with amounts of alkali insufficient to produce complete saponification; (4) use of Twitchell reagents; (5) use of lipolytic enzymes, and *saponifying*—(6) cold saponification; (7) pan boiling; (8) lime process.

Before describing these processes, some generalities concerning the factors influencing the rate and completeness of hydrolytic reactions may be emphasized; saponifying processes imply completeness of reaction.

Although fats are considered as insoluble in water, there is nevertheless a slight mutual solubility which increases perceptibly with increase in temperature. Conflicting views have been expressed on the question of whether the initial stages of hydrolysis of a melted fat (i.e. oil) take place at the interfaces between the oil and the water, in the oil-in-water solution, or in the water-in-oil solution. Recent views expressed by Lascaray (1939b) favour the last-mentioned reaction; but in each case the hydrolysis would be assisted by increased temperature and by agitation, the latter to provide an interfacial area between the two liquids sufficient to allow a reasonable rate of reaction or mutual solution.

Kaufmann and Keller (1937) have demonstrated that an increase in temperature increases the *rate* but not the equilibrium completeness of hydrolysis of a fat by water alone, when other conditions (e.g. agitation) are equal:

> 140°C.(284°F.)........ 3.6 per cent hydrolysis in 20 hours,
> 77.5 per cent (maximum) in 108 hours;
> 185°C.(365°F.)........77.5 per cent (maximum) in 20 hours;
> 205°C.(401°F.)........ 3.1 per cent hydrolysis in 2 hours,
> 77.5 per cent (maximum) in 11 hours.

The *completeness* of the hydrolysis is thus independent of the temperature, but is increased by an increase in the ratio of water to oil:

> Water:oil = 1:6 (Temp. 205°C.)...maximum hydrolysis 68.3 per cent;
> Water:oil = 1:3 (Temp. 205°C.)...maximum hydrolysis 77.5 per cent;
> Water:oil = 1:2 (Temp. 150°C.)...maximum hydrolysis 84.9 per cent.

Lascaray (1939a) investigated the effects of small amounts of alkaline catalysts on the rate and completeness of hydrolysis. In carrying the ratios of water to oil beyond the limits investigated by Kaufmann and Keller, the following data, obtained when using 0.5 per cent caustic soda and a temperature of 185°C. with uniform agitation, show a further increase in completeness of the reaction at equilibrium:

> Water:oil = 3:5 gave 90 per cent hydrolysis in 8 hours;
> Water:oil = 1:1 gave 94 per cent hydrolysis in 8 hours;
> Water:oil = 2:1 gave 95 per cent hydrolysis in 8 hours.

Increase in the amount of catalyst caused an increase in the *rate* of hydrolysis; 1 per cent caustic soda gave substantially the same degree of hydrolysis

in 5 hours as 0.5 per cent gave in 8 hours. The *completeness* of the reaction was slightly increased by the additional amounts of catalyst, an effect due to a displacement of the equilibrium by the combination of some of the free fatty acids to form soaps. This effect with apparently small amounts of catalysts is greater than would at first appear, because of the great difference between the low molecular weights of the usual hydrolytic catalysts and the high molecular weights of fatty acids. Thus, for a typical fish oil, the per cent of fatty acids fixed as soaps are as follows, using of each catalyst an amount equal to 1 per cent by weight of the oil:

Zinc oxide	Magnesium oxide	Calcium oxide	Lithium hydroxide	Caustic soda	Caustic potash
7.2	14.5	10.1	12.2	7.3	5.2

The foregoing catalysts are arranged in the increasing order of efficiency found by Lascaray (1939a) when investigating their promotion of the autoclave hydrolysis of an animal fat at 185°C. (365°F.). Zinc oxide increased the rate of reaction much more than any of the others, a result corresponding with the observation that water is very much more soluble in fat in the presence of zinc oxide than in the absence of a catalyst.

Not all of the fat-splitting processes to be described are suited to the treatment of all marine animal oils. In any process involving a temperature over 300°F. for an appreciable length of time, the highly unsaturated fatty acids of many fish body oils such as pilchard, herring and menhaden oils and some fish liver oils are prone to undergo oxidation, polymerization or even partial decomposition, with consequent darkening and acquisition of other undesirable properties. The fatty acids of marine mammal oils such as whale oil are not so subject to such changes. Fish oils that have been hydrogenated prior to hydrolysis or saponification undergo splitting with little if any alteration of their component fatty acids. If the fatty acids are to be used as such, any dark colour acquired during the fat-splitting is usually removable in a secondary purification by distillation or other means.

(i) AUTOCLAVING WITH STEAM ALONE

This method requires such high temperatures that it is not generally suitable for the treatment of fish oils. Whale oil and hydrogenated fish oils are somewhat more amenable to the process, but the fatty acids recovered have a tendency to be dark in colour. The fat is heated with live steam at 200 to 220 pounds pressure per square inch corresponding to temperatures of about 388° to 395°F. Water up to 30 per cent of the weight of the fat is sometimes added prior to the introduction of steam. The steam is best distributed by fine jets, and a slight continuous escapement facilitates agitation. A variation of this process involves blowing superheated steam into the fat preheated to about 570°F., at which temperature both the fatty acids and the glycerol are volatilized with the steam and condensed separately in the order given. The Hoffman fat-splitting reaction is a continuous process involving hydrolysis at 430° to 500°F. of a water-emulsified purified fat under 300 to 900 pounds pressure per square inch. The product is then passed into a high-vacuum expansion zone where the fatty acids distill, whereas the unsaponified residues remain liquid. Splitting to the extent of 99 per cent is claimed, with easy recovery of glycerol.

(ii) AUTOCLAVING WITH ACIDS

Hydrochloric and sulphuric acids have been employed for the splitting of low-grade fats. With hydrochloric the difficulty of maintaining contact between the acidulated water and the

fat tends to hinder the reaction, which becomes very slow after splitting is 75 per cent complete. Sulphuric acid has an emulsifying effect which favours mixing and greater completeness of reaction, but the fatty acids produced are apt to be sulphated and dark in colour. The fatty acids of unsaturated fish oils are particularly prone to sulphation which renders this process unsuitable for such oils unless sulphated and otherwise altered fatty acids are desired. The oil or fat is first dried by heating for some time at a temperature of about 250°F., 6 to 7 per cent of concentrated sulphuric acid is then stirred in, and the temperature maintained at 230° to 250°F. by passing in dry steam until the splitting is complete (8 to 10 hours). The fatty acids are boiled with water several times, and distilled with steam under reduced pressure for purposes of purification. Recovery of glycerol is low.

(iii) Autoclaving with insufficient alkali for complete saponification

This method, though widely used for animal and vegetable fats, is not particularly suitable for highly unsaturated fish oils. The autoclave is charged to about 75 per cent of its capacity with a mixture of 75 per cent fat, 21 to 22 per cent water, and 3 to 4 per cent calcium, barium or magnesium oxide with or without the addition of 0.5 to 1 per cent of "zinc dust" (mixture of metallic zinc and zinc oxide), which serves to preserve the resultant fatty acids from undue discoloration. Steam at 100 pounds pressure per square inch is supplied to raise the temperature to about 285° F. After 5 hours the hydrolysis is about 90 to 93 per cent complete, and after 12 hours, 98 to 99 per cent complete. As previously pointed out, a considerable portion of the liberated fatty acids will be fixed as alkali-metal soaps. These fatty acids may be recovered by boiling the soaps with dilute sulphuric acid. Glycerol recovery in this process is high.

(iv) Hydrolysis by Twitchell reagents

The Twitchell process is a truly catalytic one, employing as catalyst any one of a number of sulphonated compounds collectively known as "Twitchell reagents" such as those described on page 109. It is suitable for the treatment of all but the most highly unsaturated marine animal oils. Advantages are cheapness in respect to amount of reagents required, economy in steam consumption and favourable recovery of glycerol; a disadvantage is the lengthy reaction time and a consequent tendency to produce discoloured fatty acids. In one form of the process, no autoclave is required and wooden tanks may be employed. Up to 100 tons of material may be treated at one time, the charge consisting of clarified fat or oil with 40 to 100 per cent of its weight of water, plus 0.5 to 1.0 per cent of Twitchell reagent, based on the weight of the fat. Gentle mixing at 212° F. is maintained by passing in open steam and the hydrolysis is practically complete in 24 to 60 hours depending on the nature of the fat. The addition of from 0.5 to 2.0 per cent of 75 per cent sulphuric acid to the mix is claimed to accelerate the hydrolysis. It is also considered advantageous to interrupt the hydrolysis when about half completed, to allow settling, to run off as much as possible of the aqueous layer containing glycerol, and to resume the heating after making up to volume with water. A Twitchell reagent sold under the name of "Kontakt" (a sulphonated petroleum product) effects practically complete hydrolysis when added in amounts of 0.5 to 0.75 per cent of the weight of the fat. This reagent may be obtained in an acid form, or in a neutral form requiring the addition of sulphuric acid in amounts as stated above. There recently has been described a Twitchell process involving autoclaving with steam at 266° to 284° F. with the addition of sulphuric acid, whereby hydrolysis is practically complete in 6 hours. United States patent 1,976,376 describes a modified Twitchell process in which the passage of an alternating electric current of 0.25 amperes at 3 to 5 volts greatly decreases the time of hydrolysis at 212° F. It is claimed that the reaction is 77 per cent complete in 3 hours, 91 per cent in 6 hours and total in 9 hours.

(v) Hydrolysis by lipolytic enzymes

This process utilizes the natural enzyme of the castor bean and is suitable for all types of marine animal oils as it avoids subjecting the oil or fatty acids to high temperatures; glycerol

recovery is satisfactory. Disadvantages are cost and variability in activity of the enzyme preparation, the care necessitated in preparation of the same, the long duration of the reaction, and the circumstance that the degree of hydrolysis seldom exceeds 90 per cent. The clarified oil is emulsified by an air blast with about 50 per cent of its weight of water and 7 to 12 per cent of its weight of prepared enzyme in the form of a cream. The mixture is allowed to stand for 36 to 48 hours at 68° to 86° F. The emulsion is then broken by passing in steam, with the addition of a little dilute sulphuric acid if the emulsion is persistent.

The foregoing methods (i) to (v) are primarily for the production of free fatty acids and glycerol. The fatty acids may be purified by intermediate formation of a soap, or more generally by distillation with steam under reduced pressure. The most modern distillation methods employ a continuous counter-current passage of the crude fatty acids into superheated steam under high vacuum. The distillation temperature of the steam-fatty-acid mixture may thus be reduced to between 300° and 400°F. For further details of the various hydrolytic processes and the recovery of fatty acids and glycerol, patent literature and technological books on the subject should be consulted.

(vi) COLD SAPONIFICATION

In this process the exothermic nature of the reaction between caustic alkalies and fats is utilized to supply the heat necessary to complete the saponification. It is suitable for marine animal oils, and is used for the production of certain types of soaps where the recovery of glycerol is unimportant or undesirable. The fat is heated to 104° to 140° F. in an open vessel and the predetermined amount (or a very slight excess) of strong caustic soda or potash solution is run in with rapid agitation. When the emulsion which forms has become sufficiently viscous, it is cast into moulds or frames and allowed to stand in a warm room, where the reaction proceeds for a further 24 to 48 hours with some spontaneous elevation in temperature. A modification involves mixing the fat with the theoretical amount of powdered caustic alkali at the above temperatures, and then initiating the reaction by the addition of an amount of water less than the weight of alkali used. Another modification, employing caustic and alcohol, and particularly suitable for the recovery of the vitamin-containing unsaponifiable portion of fish body and liver oils, is described on page 306.

(vii) PAN-BOILING PROCESS

This is the process most commonly used for the manufacture of soap from any fat, including suitable clarified or hydrogenated marine animal oils. Many variations and refinements of the process are in use, but the procedure in general is to raise the temperature of the fat to about 212° F. by passing in open steam. The predetermined amount (or a very slight excess) of caustic soda or potash, as a 10 to 32 per cent solution depending on the method used, is simultaneously and cautiously run in to secure emulsification without allowing any temporary local excess in concentration of alkali which would tend to break the emulsion and delay saponification. The gentle ebullition with steam is continued for several hours and the reaction is complete in 12 to 24 hours. Purification of the soap and recovery of glycerol proceed according to the purposes for which they are intended. Continuous processes for alkali saponification have already been metioned on page 110.

(viii) LIME PROCESS

This process is analogous to the preceding one except that saponification is effected by the use of a thick cream of slaked lime, in amount 50 per cent in excess of that required for total reaction with the fatty acids produced. Saponification is complete in about 12 hours. It is much used in preparing stock for greases and is applicable to many types of marine animal oils. In a modification known as the Krebitz process, the lime cream is run into the fat at about 100°

to 120° F., and steam is passed in until a stable emulsion is produced without allowing the temperature to exceed 203° F. The batch is then allowed to stand for 24 to 36 hours. In either process, the lime soaps may be converted into free fatty acids by boiling with dilute sulphuric acid, or directly into sodium or potassium soaps by boiling with a solution of the corresponding alkali carbonate. Glycerol recoveries are high.

(b) HYDROGENATION

Sabatier's classical investigations laid the foundation for modern hydrogenation processes. The possibility of applying the reaction in liquid media was suggested by LePrince and Siveke (Ger. pat. 141,029, 1902) and Normann (Brit. pat. 1,515, 1903) and from these suggestions the progress of industrial hydrogenation of oils has been most rapid. The earliest methods stressed the intimate mixing of oil, catalyst and hydrogen, but it is now known that it is the intimate contact of oil and catalyst that is necessary, since hydrogen is appreciably soluble in oil.

In industrial hydrogenation the source of hydrogen is of vital importance. It must be cheap and either produced with, or refined to a high degree of purity. For research or small plants the hydrogen may be obtained from cylinders of the compressed gas, which is usually prepared by the electrolysis of water and is very pure. However, for large scale operations it is necessary to secure a more economical source.

The methods of preparing industrial hydrogen are treated in considerable detail by Ellis (1930) and Taylor (1921), and may be classified as follows: (1) From water gas and steam (water gas catalytic process); (2) from water gas by liquefaction; (3) from hydrocarbons, by (a) thermal decomposition, or (b) action of steam; (4) by electrolysis of water; and (5) from steam and iron.

The type of plant used depends upon local conditions, but with cheap electrical power the electrolytic cell is probably the most satisfactory. The hydrogen produced is of high purity and requires a minimum of purification before use.

The two most important types of cell are the Knowles and the Bamag-Zdansky. In the former the electrodes, surrounded by asbestos sleeve diaphragms, dip into a 15 per cent solution of caustic soda; the gas is collected by "bells" inverted over them and is conveyed to storage by pipes. These pipes are designed to remove spray from the gas and return it to the cell. The Bamag-Zdansky cell using the filter press principle is very efficient and, except for occasional washing of the electrodes, the cells will operate for long periods without attention.

There are four main methods in use in hydrogenation plants:

(i) BY MECHANICAL AGITATION

This type of plant uses a steel tank fitted with openings suitable for inspection, introduction and discharge of oil and injection of hydrogen, and with coils for use with steam under pressure for initiating the reaction. In addition there is provided a suitable mechanical agitator. The hydrogen is admitted slowly as required to maintain the desired pressure, and mixing is provided by the agitator. The packing glands required by this type of hydrogenator introduce the possibility of leakage of hydrogen with its attendant loss and danger.

(ii) BY AGITATION WITH HYDROGEN

The type of equipment is similar to that used in mechanical agitation except that no provision is made for stirring. The hydrogen is introduced in a strong

blast through a system of distributing pipes bearing fine holes to secure the most efficient agitation of the oil and catalyst. The hydrogen is withdrawn from the top of the tank and recompressed for further use. There are no packing glands used in this system, thus reducing the possibility of loss of hydrogen.

(iii) BY CIRCULATION OF OIL AND CATALYST

The Maxted Thompson process (Maxted 1921) consists essentially of causing the oil and catalyst mixture to flow downward through a tower counter-current to the stream of hydrogen. This is achieved in a tower fitted with baffles that throw the oil alternately outward and inward, and the oil-catalyst mixture is re-cycled by a pump which removes the oil from the bottom of the tower and sprays it in at the top. The hydrogen is withdrawn from the top of the tower, recom-
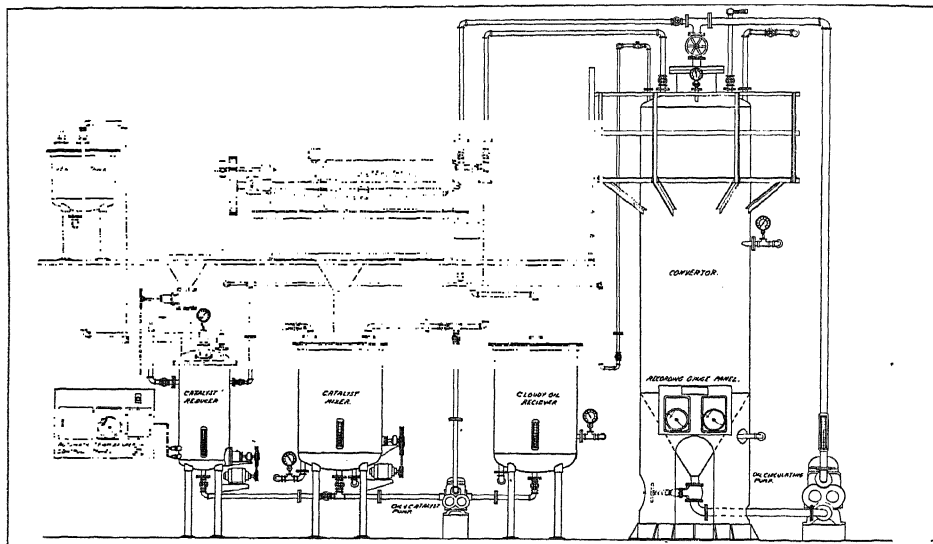
FIGURE 62. A typical hydrogenation plant (Courtesy Wurster and Sanger, Inc.).

pressed and introduced at the bottom. The tower is surrounded with a steam jacket to provide the heat necessary to initiate the reaction, but, owing to the intimate mixing, the temperature may be raised to 170°C. (338°F.) by the heat of the reaction once it starts.

According to the Testrupp method (Brit. pat. 7,726, 1910) the preheated oil and catalyst are sprayed into the reaction chamber in which an atmosphere of hydrogen is maintained under suitable pressure. The oil and catalyst are with-drawn from the bottom of the chamber and re-cycled until the desired hardening is obtained.

With all the methods using loose or powdered catalysts, hardening is followed by filtration while the hydrogenated fat is still liquid, in order to remove the

catalyst. The recovered catalyst frequently may be used again for further hardening if the oil has been highly purified, and spent catalysts may be recovered and re-prepared if nickel is expensive. In certain cases the spent catalyst has been used in a preliminary treatment to remove catalyst poisons from the oil before beginning the hydrogenation.

Figure 62 shows a typical hydrogenation plant with circulation as used for marine animal oils. In this plant the catalyst is prepared by the wet-reduction method from nickel formate which is replacing dry reduction. Since the oil is partially hydrogenated during the reduction of the catalyst, it may be cast into blocks and only as much as required cut off for use with any batch of oil, or it may be transferred directly from the reduction chamber to the catalyst-mixing tank. Here it is mixed with part of the charge before being introduced into the converter with the rest of the oil.

The oil in the converter is circulated by a pump and is heated to the starting temperature. The tank is evacuated to remove air and moisture, and hydrogen is then blown through the charge while the pressure is allowed to reach 60 pounds per square inch. Once the reaction begins, it is necessary to cool the charge as the reaction is exothermic. This is accomplished by internal cooling coils or external heat exchangers.

After hydrogenation is complete as determined by the refractive index or melting point, the hydrogen is shut off and the oil cooled by circulation until the temperature is sufficiently low for filtration. The charge is pumped to the filter presses, and when filtration is complete the nickel is scraped out and returned directly to the catalyst-mixing tank where it is introduced into the next batch of oil for hydrogenation. The oil from the filter press may be passed to the deodorizer if necessary to prepare it for use as an edible fat.

(iv) WITH STATIONARY CATALYST

This process, which was described by Bolton (1927) and Lush (1927), is known as the "T.R.W. process of continuous hydrogenation", and is controlled by the Technical Research Works Ltd., London, England. It is a continuous process and utilizes a rigid catalyst which eliminates the necessity of filtering the oil which is always required when powdered catalysts are used. The catalyst was originally made up of pure nickel turnings held in monel metal cages, but the latest type consists of pure nickel elements fitted together to form self-supporting rigid blocks. These are activated by anodic oxidation followed by reduction in hydrogen. The oxidized catalysts are placed in a drawn steel tube, or reactor as it is termed, in which they fit tightly and are reduced in the hydrogenation plant itself. In the earlier type of plant a number of tubes were arranged in series, but in the latest type only one tube or reactor is used. After the reduction of the catalyst the plant is ready for hydrogenation.

Figure 63 shows a drawing of the essential parts of such a plant. It represents the latest type of single reactor unit, A indicating the reactor containing 12 of the new type block catalysts as shown at CCC. The reactor is surrounded by a heating jacket and has also an internal heating unit (not shown in the drawing), to provide heat for the reduction of the catalyst and for initiating the reaction. The oil is pumped into the heat exchanger B which serves as feed vessel and preheater, from which the oil is fed into the system through O by means of hydrogen pressure supplied at H_1. Hydrogen is also admitted with the oil to the reactor through H_2.

Oil can be admitted either into the top of the reactor through O_1, dripping down through the catalyst and leaving at O_2; or alternatively, it can be introduced at the bottom of the reactor through O_3, flowing up through the catalyst, filling the reactor and overflowing at O_4. In either case the oil and excess hydrogen pass out together into the separator S where the excess

hydrogen separates from the hydrogenated oil and passes out through E while the oil flows down through the cooler D and is obtained at F.

The degree of hardening is controlled by the temperature and pressure but mainly by controlling the rate of flow of oil through the plant.

The plant may be extended to include more units as operating conditions warrant.

The process is continuous, and reactivation is simple and cheap. The plant is operated successfully and economically in small units and, since it is continuous, with no moving parts except the feed pump, it features economies in heat and power.
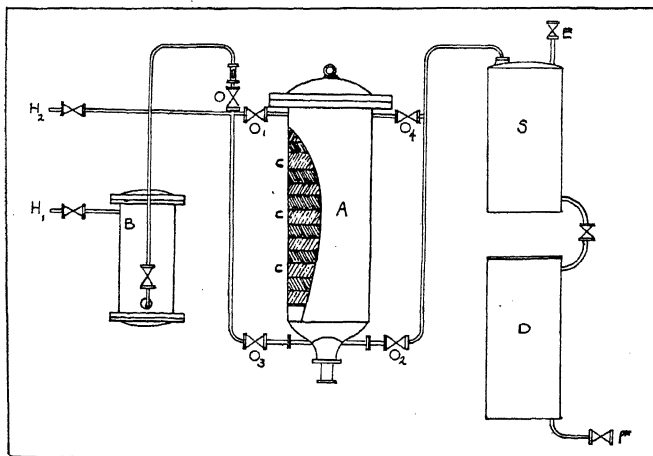
FIGURE 63. Essential parts of a continuous hydrogenation plant.

(c) OXIDATION

(i) OXIDATION PROCESSES

A boiled oil is a drying oil with which has been incorporated a suitable amount of drier by means of a heat treatment and, depending upon the product desired, which has been blown for some time. Blowing during the incorporation of the driers produces a product that is partially oxidized and polymerized and that will dry more quickly than raw oil to give harder and more lustrous films. This is most important in varnish technology. The length of time of blowing depends upon the viscosity desired.

The process in general consists in raising the temperature of the oil to about 105°C. (220°F.) and gradually adding the drier with agitation by a stream of air; the temperature is maintained until a clear solution is obtained. As this process gives a product that is dark in colour owing to extensive oxidation, a small quantity of oil is frequently incorporated with the driers, which are then mixed with the main portion at as low a temperature as possible, usually not above 95°C. (200°F.). In this manner a product of lighter colour is obtained.

The driers usually added are lead oxide, cobalt oxide or acetate and manganese oxide or borate. The newer procedures consist in using the soluble soaps, resinates, naphthenates and linoleates of the foregoing metals. They are soluble

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in the oil and may be incorporated at much lower temperatures to produce products of light colour.   Heat is usually applied by means of closed steam coils to prevent the undue darkening caused by local overheating which would occur with direct firing.

In order to produce a cheaper product, the drier is sometimes added to the oil at about 35°C. (95°F.) and the mixture vigorously agitated by an air blast to obtain a homogeneous mixture.   During blowing the oil must be cooled to prevent excessive rise in temperature.   Oils prepared in this way are referred to as "bung-hole boiled oils".

(ii) BLOWN OIL

These oils are produced in a similar manner to boiled oils but the blowing process is continued longer to make a more highly polymerized oil of high viscosity.   The oil is blown with air at a temperature of about 90°C. (194°F.), and the oxidation soon becomes so rapid that the temperature rises to about 120°C. (248°F.), whereupon cooling water is circulated through the coils to prevent further rise with consequent darkening.   A vigorous current of air is necessary to produce a viscous oil in a short time and also it assists in carrying off some of the volatile acidic oxidation products.   By careful working, an oil may be obtained with an acid value below 10.   Being partly oxidized, these oils dry rapidly, but the film formed is less durable than from oils polymerized by heat alone. However, blown oils wet certain pigments such as white lead and the ochres better than does raw or boiled oil.

Pilchard oil may be blown satisfactorily to produce oils of high viscosity or solid gels, but it does not body as rapidly as linseed oil, several days at 125° C. (257° F.) being required to produce a solid gel.   When blowing was carried out at 250° C. (482° F.), the apparent molecular weight of the oil increased steadily during the course of 22 hours.   The viscosity increased very slowly until the tenth hour when the values suddenly increased to a final value of 28.4 poises.   During the preliminary heating before blowing was started, the acid value rose from 1.5 to 8.1, but during the vigorous blowing it dropped until it reached an almost constant value of 3.   Further data concerning the oxidations involved may be found in Section 5 I (c) (oxidation).

(iii) SHOWER BATH AND SMACKER PROCESS

This is a modification of the blowing process and is carried to the limit of oxidation by air with the production of a rubbery mass.   The oil containing driers is maintained at 50°C. (122°F.) and passed in a shower through the air from the perforated bottom of a tank or trough.   This is collected in a lower tank and re-percolated until it becomes too thick to re-cycle, when it is transferred to a steam-jacketed agitator or "smacker".   Here it is violently agitated with a strong stream of air at 55°C. (131°F.) until it becomes a crumbly mass, when it is stoved or heated for several days at 40°C. (104°F.).   The product is used in the manufacture of linoleum.

(iv) SCRIM OIL

Another method of securing the "linoxyn" or oxidized solid oil is to permit the oil containing driers to flow over a mass of loose cotton fabric or "scrim", suspended in a room maintained at 38°C. (100°F.).   Because of the large amount

of surface exposed, the oil dries as it flows over the cotton and that which drips from the fabric is collected and the process repeated until a coating of half an inch of solidified oil is obtained. This is stripped off and shredded through rolls.

(v) TAYLOR-PARNACOTT METHOD

This method consists in blowing boiled oil containing lead and manganese driers with air for several days at about 150°C. (300°F.), during which process a dark-coloured product is obtained. This is divided into smaller fractions and heated for six or seven hours at about 250°C. (482°F.) until the mass solidifies. Oxidation and polymerization proceed together and the product is dark and tacky.

Menhaden and whale oils blown to the proper consistency by this method are used to a considerable extent for linoleum preparations.

(vi) OIL GELS

Resins of the abietic acid type may be incorporated with drying oils and driers, and, when blown at about 150°C. (300°F.), produce an oil gel which may be used with fillers and pigments of various kinds in the production of floor tile and roofing compounds. Pilchard oil has shown promising results in the production of this type of material, giving a firm thermoplastic gel of good binding power. Preparation of tiles from this type of gel permits the use of lighter colours than when fatty acid pitches are used.

(vii) MISCELLANEOUS

Oil tanning of leather may be considered essentially an oxidation process. Probably the first step is the oxidation of the oil and it is the oxidized oil that does the tanning. Pilchard oil has been used very successfully in tanning small skins by direct application after a preliminary pickling. Precautions must be taken to prevent overheating by rapid oxidation of the very unsaturated oil with resultant damage to the hide. This is particularly true if traces of the oxidation catalysts, copper or iron, are present.

Oxidation processes also enter into certain methods of bleaching as discussed in Section 8 I (c).

(d) BODYING OILS WITH HEAT.

The treatment of drying oils with heat in the presence or absence of other materials such as oxygen and catalysts of various kinds is done to produce thickened oils, variously called "stand-oil", lithographic varnish, etc. These are used primarily for the manufacture of domestic enamels, machinery enamels, lithographic inks, waterproof coatings, certain types of varnishes and patent leathers. The methods used for the manufacture of these thickened oils vary with the type of product desired.

(i) TOP-FIRING

In this process bodied oils are made by heating the oil in open kettles until the flash point of the vapours is reached. The vapours are ignited and heating

continued until the desired thickness in the oil is obtained. If carefully made, a top-fired oil will be lighter in colour than one made in an open kettle without top-firing, and will find preference in the manufacture of lithographic inks, particularly those used for copperplate printing.

(ii) OPEN KETTLES

Although being superseded by more modern equipment, these are still quite generally used for the production of stand-oils. They are made of copper, enam-elled iron or aluminium, the latter material being the most satisfactory in giving light-coloured oils. The kettles are set over coke fires, or in more modern instal-lations, gas or oil fires, and the oil heated to about 260° to 290°C. (500° to 560°F.) until the desired thickening has taken place. Considerable decomposition takes place and the kettles are equipped with hoods to remove the fumes which should not be allowed to condense and fall back into the oil. The losses due to decom-position vary from about 3 to 15 per cent depending on temperature and length of time of heating; these losses are slightly higher for fish oils than for linseed oil. During heating in these open kettles a certain amount of oxidation occurs and some authorities claim the product is superior to that made in closed vessels as it dries more quickly; however, it apparently gives less stable films. Blown and partly oxidized oils wet pigments better than those thickened in the absence of air and consequently are added to certain pigments during grinding. For the preparation of enamels and varnishes, however, Meister (1932) claims that oils thickened in the absence of air in closed vessels are much superior to the open-kettle type of stand-oil.

(iii) INDIRECT HEATING

This is done in covered kettles and for the production of stand oils it is rapidly replacing the open-kettle type of equipment. In the new equipment provision is made for the rapid and uniform heating of the oil, either by heating coils through which superheated steam or hot mineral oil is circulated, or by means of external electric resistance coils. Very precise control of the temper-ature can be obtained and the control can be automatic. In addition, covered kettles of oil-resistant material such as aluminium or nickel-iron alloys, together with the use of inert gases, allow production of very pale oils of low acid value. The use of such equipment is to be recommended for the heat-treatment of highly unsaturated fish oils which usually darken very quickly if heated in the presence of air.

British patent 448,956 describes an apparatus in which drying oils are poly-merized by rapid and continuous passage through a heated and restricted conduit of small cross-section in order to heat the oil rapidly to the temperature of poly-merization. The hot oil is then circulated through another conduit maintained at the polymerizing temperature, after which the oil is rapidly cooled to arrest polymerization. The method is continuous and, since the oil is heated very rapidly to the required temperature, it is claimed that the formation of decom-position products is reduced to a minimum.

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(iv) DISTILLATION

Various methods using this process have been introduced recently to improve the quality of stand-oils; these methods include both high-vacuum or short-path distillation and steam distillation under reduced pressures. Typical of the first method is the process disclosed in British patent 422,941, in which the polymerized oil is distilled in a very high vacuum, with the condensing surface in close proximity to the evaporating surface, whereby low-molecular non-polymerized glycerides and free fatty acids are removed. Dutch patent 36,952 describes a process in which the product of polymerization of fatty acids or saponified fatty oils is separated from non-polymerizable acid either by steam distillation at high temperatures or by vacuum distillation. The distillation residue of polymerized fatty acids is then esterified and used as a stand-oil. U.S. patent 1,915,260 seeks to polymerize oils and to reduce their acidity by circulating the oil in a closed path which is heated sufficiently to cause polymerization and vaporization of the free fatty acids. The oil is then sprayed in such a manner that the sprayed particles descend on the surface of the oil in the closed path, the vapours being withdrawn through the pump which maintains a high vacuum within the system. The oil is continuously recirculated through the system until the desired polymerization has been effected.

G. Kaempfe (1936) discusses the production of stand-oils from marine animal oils by a distillation process that appears to be based on the original French patent 445,565 issued in 1912 to G. Kaempfe. According to this patent the oil is heated for a short time at 235° to 240°C. (455° to 464°F.) at ordinary or diminished pressures and then steam at 375° to 400°C. (707° to 752°F.) is blown through for 25 to 30 hours, the temperature of the oil being kept below 260°C. (500°F.). The effect of the process is to expel the saturated fatty acids or their glycerides and to polymerize the residual unsaturated fatty acids. The residue is stated to form a satisfactory substitute for boiled linseed oil. According to the experience of Brocklesby and Denstedt (1934) the above procedure entails a considerable loss of unsaturated fatty acids in the distillate and they prefer to polymerize a fish oil at 350°C. (662°F.) for 1 hour in an inert atmosphere and then to distil with superheated steam, maintaining the oil at a temperature of 300°C. (572°F.). Distillation is continued until the residue thickens, but is stopped before actual gel formation takes place. The polymerized residue is cut with thinners and used as a stand-oil. Detailed information on the properties of this material when made from Canadian pilchard oil will be found in Section 9 I (d) of this Bulletin.

(v) HIGH PRESSURE

Methods of this type for the production of stand-oils have been patented, but no data have been published recently regarding the properties of the resulting products. In 1921 Coffey showed that linseed oil, polymerized under pressure at constant temperature, developed less free fatty acids and showed a much lighter colour than when polymerized at atmospheric pressure in open vessels.

He attributed the lower free-fatty-acid content to the fact that an equilibrium would be set up between the small amount of moisture present and the glycerides, since any free fatty acids formed could not escape from the system. Also, under pressure heating in the absence of oxygen, the glycerine formed could not decompose into acrolein and water as it undoubtedly does during the heating of oils in the presence of air. Consequently only the water originally present in the oil would be available for hydrolysis.

British patent 452,039, issued to the Imperial Chemical Industries Ltd., describes how drying oils are polymerized at pressures of 500 atmospheres and over. The oils or free fatty acids are first degassed to remove moisture and dissolved oxygen. In an example given in the patent, alkali-refined linseed oil is heated at 325°C. (617°F.) under 3,000 atmospheres for 1.5 hours, whilst linseed fatty acids are heated at 280°C. (536°F.) at the same pressure for 3 to 4 hours. After polymerization the fatty acids are esterified and the product used in varnish manufacture.

(vi) CATALYTIC AGENTS

These for use in the polymerization of drying oils are the subject of many patents of which the following are a few examples. British patent 461,853 describes a process in which the drying oil, dissolved in a halogenated hydrocarbon solvent, is polymerized at room temperature in the presence of a halide catalyst of the Friedel-Craft type such as boron fluoride. According to United States patent 1,986,571, a drying oil of high dispersive power and with a reduced tendency to become yellow is produced by the heat treatment of oils in the presence of 0.04 to 0.2 per cent of sulphur, selenium or organic compounds of these elements, and by then removing substantially all of the sulphur or selenium from the product by heating with a finely divided heavy metal or its oxide such as copper, zinc oxide or lead oxide. The polymerization of fatty oil in the presence of heavy metals dispersed electrically in an organic medium miscible with the oil is covered by British patent 444,440. Dispersions of cobalt, iron, manganese, etc., in butyl alcohol are suitable, and drying, semi- or non-drying oils may be treated. A stand-oil may be prepared from fish oil, according to the Japanese patent 100,462, by heating the oil in a closed vessel at about 275°C. (527°F.) in the presence of 0.4 to 0.5 per cent sodium bisulphite. Kozlov, in the Russian patent 34,669, claims that the heat polymerization of drying oils is accelerated by the addition of 0.2 to 1 per cent of mercaptobenzothiosole and 0.1 to 0.5 per cent of diphenylguanidine in the presence or absence of calcium resinate, whilst Scheiber in British patent 319,218 makes the same claims for benzidine, diphenylamine and other amines. The use of sulphur dioxide and sulphur chloride in the preparation of stand-oils is covered by many patents. Vulcanized oils increase the water-resistance of paints, and, since they are soluble in resins, they may be used for reinforcing varnishes. According to Heublyum (1935) linseed oil blown in the presence of 14 to 16 per cent sulphur chloride with subsequent addition of cobalt or manganese driers gives firm-drying water and acid-resisting paints. It is preferable, however, to polymerize or blow the oils first in the pre-

sence of driers, to cool and then to continue the treatment after the addition of but 1 to 3 per cent of sulphur chloride. It is claimed that the latter method gives superior paint oils.

(e) SULPHATION AND SULPHONATION.

As stated on page 134, the processes of sulphation and sulphonation are closely related and both may take place simultaneously during treatment of fatty compounds with concentrated sulphuric acid, depending upon the conditions of the treatment. This treatment will be referred to here as "sulphation" since this reaction predominates, despite the fact that the products are generally termed "sulphonated oils" in technical practice.

The properties of a sulphated oil will vary greatly, depending upon the nature of the original oil, the nature and amount of its impurities (particularly the mucilaginous and albuminous impurities containing nitrogen), and the nature of the sulphating process. For an original oil of given properties, the properties of the sulphated product are influenced by the following conditions of processing: (i) strength of the sulphuric acid, (ii) proportion of sulphuric acid to oil used, (iii) rate of addition of sulphuric acid to oil, (iv) temperature of reaction, and (v) degree of mixing.

(i) STRENGTH OF SULPHURIC ACID

Technical sulphuric acid containing about 93 per cent of H_2SO_4 (66° Baumé) is usually termed "concentrated" and is frequently used in sulphating oils. For sulphating blubber, cod, menhaden, pilchard and herring oils intended for leather and fur industries, a weaker acid (55° to 60° Baumé or 70 to 77.5 per cent H_2SO_4) is recommended, as some oils that tend to char with too strong acid may be successfully sulphated with weaker acid. For sulphating mono unsaturated fatty acids such as oleic, sulphuric acid containing more than 93 per cent H_2SO_4 is sometimes used. Pure sulphuric acid (100 per cent H_2SO_4) or fuming sulphuric acid (containing dissolved sulphur trioxide) tends to increase the ratio of sulphonated to sulphated products.

(ii) PROPORTION OF SULPHURIC ACID TO OIL

In two common sulphating processes to be described below, the weight of acid is 22.5 and 27.5 per cent of the weight of the oil. In thus treating oleic acid, a product containing between 5 and 7 per cent of combined SO_3 as sulphuric half ester is obtained. In experiments using 70 per cent by weight of sulphuric acid, the combined SO_3 content of sulphated oleic acid was not materially increased (Sunderland 1935); but by employing almost equal weights of oleic acid and pure sulphuric acid and keeping the temperature below 0°C. (32°F.) the product contained 13 per cent of combined SO_3, some of which was in the form of sulphonate.

(iii) RATE OF ADDITION OF SULPHURIC ACID TO OIL

The action of sulphuric acid on unsaturated fatty oils and acids produces considerable heat and the processes may roughly be divided into two classes,

depending on whether the sulphuric acid is added slowly in an endeavour to maintain a low temperature, or quickly with a consequent considerable rise in temperature. The distinction is exemplified by the descriptions of typical "high" and "quick" sulphation processes to follow (vi). A third method, details of which are not available, may consist of a "factor" process analogous to that described for sulphurization (page 299), in which the whole amount of acid is added to a portion of the oil and the vigour of the reaction controlled by judicious addition of portions of the remaining cold oil.

(iv) TEMPERATURE OF REACTION

In general, it may be stated that low reaction temperatures (up to 35°C. or 95°F.) favour formation of a product containing a maximal amount of sulphated and sulphonated compounds with a minimum of hydroxy acids and other secondary products formed as described in Section 5 I (f). External or internal cooling coils are frequently employed to ensure such temperatures. Where these secondary products may be desired for special purposes, the temperature may be allowed to rise to 54° to 57°C. (130° to 135°F.). Many patents have been issued for modified processes allowing the use of strong or fuming sulphuric acid and rapid rates of addition without development of too high a temperature. Examples are: the use of an inert organic solvent (e.g. ethylene dichloride) to dilute the oil, the solvent later being recovered from the finished product by distillation; American patent 1,374,607 for a vacuum process wherein a volatile hydrocarbon (e.g. benzol) is added for its diluting and cooling effect through evaporation under the reduced pressure; British patents 16,577-8 for dilution of the oil by saturated fatty acids or their glycerides. In this last process, particularly recommended for fish oils (e.g. eastern tuna liver oil), it is claimed that the diluents absorb the sulphated and sulphonated products as they are formed, thus preventing secondary reactions and allowing a greater degree of sulphation.

(v) DEGREE OF MIXING

Since sulphuric acid and the fatty material are originally immiscible, efficient mixing must be employed to secure sufficient interfacial area for the reaction to proceed. As an example of the effect of mixing, it has been determined (Sunderland 1935) that for a given mixture, stirring by means of paddles rotating at 40 revolutions per minute required 5 hours for completion of the reaction; when violent (turbulent) agitation was employed, the same degree of reaction was reached in 17 minutes; when the two reactants were brought into immediate intimate contact throughout, between the relatively moving surfaces of a colloid mill, the reaction took place practically instantaneously. American patent 2,129,896 covers an arrangement for continuously passing the fatty compound as a film between relatively moving adjacent surfaces and introducing the sulphating reagent into the continuously moving film. Such procedures may be made to allow a rapid removal of the heat generated in the reaction. Once the reaction has started, efficient stirring or mixing must be continued to avoid local

overheating with its attendant danger of charring or production of unwanted secondary products.

(vi) TYPICAL SULPHATION PROCEDURES

To illustrate the later stages of the processes, typical procedures technically known as "high sulphonation" and "quick sulphonation" will be summarized from a description given by Sunderland (1935).

"High sulphonation" is frequently employed for cod and sperm oil when it is desired to obtain a product not too sensitive to the action of dilute mineral acids, which will not readily form insoluble salts with calcium and magnesium compounds, and which will retain the softening and lubricating qualities of the original oil. Such products usually have a water content of over 20 per cent and tend to stand dilution with more water without showing turbidity as is sometimes the case with "quick sulphonated" oils.

For a 300-gallon (Imperial) quantity of oil, 27.5 per cent by weight (about 760 lb.) of concentrated sulphuric acid is employed. This is added to the oil with agitation and at such a rate that the temperature of the reaction approaches but does not exceed 95° F. Assuming the oil and acid to have an initial temperature of 60° F., this addition will require from 4 to 8 hours. Reiss (1931) states that during the first 4 hours sulphate esters only are formed, while longer heating leads to the production of hydroxy acids in amounts rising with the amount of acid used. Agitation is continued for a further 5 to 6 hours or until a sample (from cod oil) gives no opalescence with water. The mixture is now quenched in about twice its volume of cold 18 per cent (10° Baumé) solution of Glauber's salt ($Na_2SO_4.10H_2O$) and agitated quietly for 5 to 10 minutes at the temperature produced by the quenching (about 104° F.). The aqueous layer separating on standing is then run off, the sulphated product is treated with a 25 per cent (31° Baumé) solution of caustic soda until almost neutralized, the aqueous layer again separated, and the oil finally "cleared" with more caustic solution. Several variations of detail, particularly in the quenching, neutralizing and clearing, are encountered.

"Quick sulphonation" is frequently employed for cod and mixed oils, and for oleic acid. It yields a product capable of being washed with water without the use of Glauber's salt to cause a separation as in the case of the former process; and since the product contains 20 per cent or less of water, it blends readily with neutral animal and vegetable oils and with mineral oils.

For a 300-gallon lot, 22.5 per cent by weight (about 620 lb.) of concentrated sulphuric acid is employed. This is added quite rapidly (during 30 minutes) to the oil, with consequent rapid rise in temperature. When the temperature reaches 130° to 135° F., the mixture is quenched by dumping into a solution of Glauber's salt as in the former method, and the remainder of the process is very similar thereto. Various other systems of quenching (e.g. use of caustic soda or potash solutions instead of Glauber's salt) are used, the amount of alkali being adjusted so as to not quite neutralize all the remaining free sulphuric acid. Depending on method of quenching, amount and temperature of settling and washings, the nature of the finished product varies in respect to content of free fatty acids, proportion of fat combined as soap, etc.

No attempt can here be made to summarize the many processes that have been described for use with special sulphating and sulphonating reagents or with individual fatty materials. Some variations have been mentioned in the present section while others are indicated under Section 5 I (*f*). British patent 199,743 states that in the sulphation of fish oils the use of finely divided iron, cobalt or

nickel as a catalyst suspended in the oil promotes the reaction at lower temperatures. German patent 610,702 describes a method of treating un-neutralized batches of sulphated oils with neutral organic solvents (e.g. benzol or carbon tetrachloride) whereby a 95 to 97 per cent separation of sulphated from sulphonated products is achieved. The sulphonated products remain in the aqueous layer while the sulphated products dissolve in the solvent, which can later be removed by distillation.

The corrosive action of sulphuric acid on sulphating equipment has been studied by several investigators. Iron and steel are attacked rather rapidly through continual removal of the protective layer of hydrated iron oxide (Welwart 1933). Average depths of corrosion of nickel, monel and inconel metals after subjection to one hundred sulphation batches containing 66° Baumé sulphuric acid at temperatures of 16° to 60°C. (61° to 140°F.) followed by water and alkali washes were found to be as follows (Friend 1939):

		Average depth of corrosion per hundred batches of:	
Metal		sulphating cod liver oil	sulphating "fish oils"
Nickel..		0.028 mm. (0.0011 in.)	0.325 mm. (0.013 in.)*
Monel..		0.013 mm. (0.0005 in.)	0.126 mm. (0.0050 in.)
Inconel.			0.460 mm. (0.018 in.)

*Local attack with pitting.

Experiments have been conducted in these laboratories to ascertain the sulphating behaviour and properties of eight commercial Canadian marine animal oils. These are discussed under Section 9 I (*m*).

(*f*) SULPHURIZATION

(i) WITH ELEMENTAL SULPHUR

Raw, cold-cleared, refined, or partially blown oils are mixed with the requisite amount of powdered or pulverized sulphur and heated in closed vessels with vigorous agitation. Uniform heating by means of a surrounding heat-transferring medium is desirable to avoid scorching as the viscosity of the mass increases. Semi-solid factices may be cooled in the reaction vessel, while solid factices are usually removed, crushed, and allowed to cool in the air.

Takano (1939) has investigated the formation of "brown" factice from herring and sardine oils under such conditions, with the results shown in table XLIII A. For both oils, the factice obtained by using smaller amounts of sulphur or lower temperatures was soft and somewhat tacky; that obtained by using more sulphur or higher temperatures was hard, brittle and of dark colour. The amount of acetone-soluble material was considered rather high for factices of satisfactory quality, a circumstances that may be ascribed to the presence of various components with conspicuously different degrees of unsaturation in these oils. Sardine oil required in general a larger amount of sulphur and showed a more rapid coagulation than herring oil under the same conditions. The prolonged heating given to the last three samples of herring oil, although too long for convenience in technical use, showed that the content of acetone-free material may be reduced to satisfactory proportions concomitant with a desired lowering of free-sulphur content.

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TABLE XLIII. Sulphurization of fish oils

A. With sulphur.

Herring oil (acid value, 0.87; iodine value, 109.3; saponification value, 188.5)

Sulphur added to oil (%)	Temperature (° C.)	Heating time (min.)	H₂S evolved (%)	Combined sulphur (%)	Free sulphur (%)	Acetone extract (%)
25	170-180	60	0.68	16.6	1.08	24.6
35	"	"	0.89	20.6	....	33.9
40	"	30	1.92	22.3	6.86	37.2
40	190-192	"	2.68	22.1	5.05	33.7
25	164-165	60	0.02	15.4	4.00	40.0
35	"	"	0.10	16.8	9.47	36.1
40	"	"	0.18	19.0	11.60	38.4
30	160-162	120	....	15.8	5.32	37.2
30	"	150	....	19.7	3.68	33.2
30	"	180	....	20.1	2.89	30.7
30	"	240	....	20.9	1.75	28.0

Sardine oil (acid value, 0.64; iodine value, 173.2; saponification value, 196.5)

20	164-165	60	0.01	13.7	1.47	46.1
25	"	"	0.04	16.8	1.96	37.5
30	"	"	0.08	18.3	3.43	28.2
35	"	"	0.15	19.6	3.78	27.1
40	"	"	0.20	20.5	5.89	29.8
20	170-173	30	0.08	13.7	1.56	38.3
25	"	"	0.12	16.7	....	30.2
30	"	"	0.26	17.9	3.31	31.2
20	180-184	"	0.19	13.5	1.78	39.4
25	"	"	0.34	15.5	2.41	34.8
30	"	"	0.36	17.2	3.02	33.9
20	190-192	"	0.22	13.0	1.84	38.6

B. With sulphur monochloride.

Oil	Relative viscosity of original oil	Iodine value of original oil	Rise in temperature of reaction (° C. per min.)	Relative viscosity of product
Sperm...........	24.2	78.5	3.3	99.9
Cod liver.........	33.9	159.0	5.6	192.8
Whale...........	39.9	131.0	5.5	218.7
Menhaden.......	45.8	142.2	12.8	284.5

Specific comparative data on the sulphurization of other fish oils with sulphur are not plentiful. The following generalizations gathered from various sources do not necesarily apply to all or any one marine oil. Brown factices are usually prepared by using 10 to 20 per cent of sulphur based on the weight of oil, and

temperatures ranging from 120° to 180°C. (250° to 350°F.) for a period of 30 minutes to 2 hours. Other variations have been mentioned on page 144. Above 180°C., and particularly above 200°C. (400°F.) hydrogen sulphide is evolved in appreciable amounts. The most suitable proportion of sulphur for the nature and degree of unsaturation of the oil, and the conditions under which this sulphur is incorporated must be determined by experiment with a view to the utilization of the product. The test for content of acetone-extractable material in the finished product is a useful guide as the content tends toward a minimum when the conditions are optimal. Sulphurized cod liver oil, used in the leather industry, is preferably prepared from an oxidized oil as this reacts with the sulphur more readily than the raw oil; the sulphur in sulphur-tanned leather will react with oxidized cod liver oil, but the product has not the same effect on leather as the originally sulphurized oil.

(ii) WITH SULPHUR MONOCHLORIDE

This liquid reagent is either added to the agitated oil at once, in which case a rise in temperature takes place which may have to be controlled by cooling, or the reagent is allowed to run slowly into the oil over a period of half an hour or so in order to control the temperature rise. The same result is achieved by diluting either reagent or oil with an inert solvent, such as carbon tetrachloride, which lends itself to ready evaporation from the finished product at low temperatures. Another important modification is the "factor" process, wherein only a portion of the total amount of oil to be treated is added to the whole amount of the reagent and the reaction is allowed to take place spontaneously until incipient gel formation or insolubility is observed; the balance of the oil is then added, thereby quenching the initial energetic reaction, and the whole is allowed to react to completion. The semi-sulphurized oil thus acts as both the dispersed phase and dispersion medium. With fish oils, an abundance of hydrogen chloride is given off, and the resulting viscous liquid, gel or solid factice is washed with water or dilute sodium carbonate solution to remove as much of the acid as possible. Any organic solvent used is then evaporated off.

Here again the amount of sulphurizing agent to be employed must depend on the nature and degree of unsaturation of the oil and properties desired in the finished product. The non-specificity of sulphur monochloride for double bonds led Harvey and Schuette (1931) to conclude that vigour of reaction and viscosity of product bear more relation to the original viscosity of the oil than to its iodine value (unsaturation) and other chemical characteristics. Their results with four marine oils (table XLIIIB), using 6.7 per cent by weight of sulphur monochloride under specified conditions, indicate the nature of the action of this reagent. Abundant evolution of hydrogen chloride took place in each case, although linseed oil and several other unsaturated vegetable oils gave no such evolution. Oleic acid was found to react more readily than some of the oils.

Takano (1939) studied the effect of sulphur monochloride on herring and sardine oils in the preparation of "white" factice by allowing the reagent to run drop by drop into the fish oil dissolved in carbon tetrachloride while the temperature was held constant (table XLIV). The product was washed to remove acidic matter, and the solvent was then removed. With the larger proportions of reagent to oil, violent evolution of hydrogen chloride occurred, with a resultant lowering of the ratio of total chlorine to total sulphur in the product, a ratio which,

according to some authorities, should approximate unity in a good factice. In general, the factice from sardine oil was superior to that from herring oil, and the most suitable amounts of reagent appeared to be 20 and 15 per cent (by volume) for the sardine and herring oils respectively. The sardine oil reacted more quickly. The factices poor in sulphur and chlorine were soft, spongy and white in colour; those rich in these elements were hard and darker in colour.

TABLE XLIV. Sulphurization of fish oils with sulphur monochloride

Herring oil (acid value, 0.87; iodine value, 109.3; saponification value, 188.5)

Reagent added (% by volume)	Temperature (° C.)	Reaction time (min.)	Total sulphur (%)	Combined sulphur (%)	Free sulphur (%)	Total chlorine (%)	Acetone extract (%)
15	15	300	12.00	8.19	1.61	10.01	9.74
20	"	60	14.08	9.30	3.27	10.22	9.91
15	30	"	9.69	9.39	0.98	10.24	9.39
20	"	40	12.35	9.46	2.49	10.46	9.46
(Sample A, commercial factice)			8.55	6.51	0.41	7.39	6.51
(Sample B, " ")			7.83	4.38	1.02	8.71	4.38

Sardine oil (acid value, 0.64; iodine value, 173.2; saponification value, 196.5)

15	15	80	10.79	7.14	1.56	7.34	14.15
20	"	50	13.52	9.56	2.01	7.72	4.57
30	"	40	17.44	10.50	4.89	8.58	4.34
15	30	60	10.69	8.10	1.69	8.53	10.82
20	"	40	12.93	9.00	2.25	9.51	5.79
30	"	30	16.16	11.52	4.58	10.03	4.12

The rate of reaction of sulphur monochloride *vapour* at room temperature on cod liver oil and fatty acid esters in thin films has been studied (Kaufmann *et al.* 1937). The absorption of the reagent was very rapid for the first 2 hours and practically ceased after 6 hours. The maximal amounts absorbed (by weight) were: ethyl stearate, 11.5 per cent; ethyl oleate, 30.5 per cent; cod liver oil, 55.7 per cent. Several vegetable oils were also investigated, but the absorption by cod liver oil was exceeded only by linseed oil (65.6 per cent). The cod liver oil film solidified at the end of 40 minutes, the linseed oil after 10 minutes. Both formed films (factices) having a lighter colour than that of the original oil, and possessing good tensile strength and tensile elasticity. White and brown factices ordinarily possess compressive elasticity only. A process for the continuous production of such films in sheets having possible commercial applications depends on the action of sulphur monochloride vapour (alone or mixed with air) on cod liver oil carried on the surface of a revolving drum (Kaufmann and Mardner 1938). Such films are transparent, resistant toward creasing, non-inflammable and unaffected by hot and cold water. They are, however, not stable toward prolonged action of organic liquids.

A test for the nature and unsaturation of animal and vegetable oils suggested on several occasions in the past depended on the vigour of reaction with sulphur monochloride as measured by the rise in temperature. Although the test has not achieved much importance, some results described by Fawsitt (1888) on certain marine oils and fatty acids therefrom (table XLV) are of interest.

The use of factices in the paint and varnish industry demands the property of causing the products to be (1) little absorbed by porous materials that are

TABLE XLV. Reactivity of some oils and fatty acids with sulphur monochloride

Material	Reagent added (% by weight)	Rise in temperature of reaction (° C. per min.)	Nature of product
Cod liver oil..........	4	13.7	Viscous liquid
" " "	6	27.3	Very sticky solid
" " "	8	34.3	Dry solid
Seal oil..............	4	4.4	Viscous liquid
" "	6	13.2	Sticky solid
" "	8	22.4	Dry solid
Whale oil............	4	9.4	Viscous liquid
" "	6	14.1	Very viscous liquid
" "	8	30.2	Dry solid
Sperm oil............	4	2.3	Liquid
" "	6	4.9	Slightly viscous liquid
" "	8	8.8	Viscous liquid
" "	10	14.2	Very viscous liquid
Oleic acid............	4	10.6	Viscous liquid
" "	6	14.9	" "
" "	8	16.5	" "
Stearic acid..........	4	0.7	Solid
" "	8	1.6	"

being coated, (2) capable of thorough drying even in thick layers, (3) capable of giving considerable film thickness with consequent better resistance to water and weathering. The use of blown oils and driers for producing factices has been mentioned on page 144, and although desirable products, sometimes liquid, are purposely made by under-sulphurizing, or blowing, or both, the opinion has been expressed (Brust 1938) that the full amount of reagent should be used to attain a greater degree of polymerization, since the larger the molecule the better the guarantee of the satisfactoriness of the product. If blowing is carried too far, too little reagent is apt to be used. Special types of varnishes (spar) and paints incorporating factices have the property of "setting" almost as soon as applied, and although one coat may not yet be "dry", a second coat can be applied very soon after. German patent 596,400 claims that the solution of factices in drying oils at high temperatures provides a suitable rust-proofing paint, while the more recent German patent 621,400 describes the solution of fish-oil factices at low temperatures for the same purpose.

The use of certain (unsaturated) fish oils for producing factices for paints and varnishes has been severely criticized on account of their tendency to liberate considerable quantities of hydrogen chloride when treated with sulphur monochloride. This evolution of acid may slowly continue in the finished product, with detriment to the adhesion of the film on metallic surfaces. This objection does not apply, however, to factices prepared from fish oils and sulphur, or to the factices prepared from fish oils by suitable modifications of other sulphurizing

processes, such as first blowing the oil with a drier, and using only 3 to 4 per cent of sulphur monochloride (Osnos and Golovistikov 1932).

(g) DISTILLATION

The mixed fatty acids obtained by the hydrolysis of fish oils consist of components showing a wide range of melting points. These mixed acids are suitable for many purposes, but in some cases fractions of narrower melting points are required. Furthermore, fatty acids prepared from relatively unsaturated oils are usually dark in colour. Decolorizing and fractionation may be obtained by distillation, and products suitable for emulsifying agents and synthetic resins, soaps and candle stock thus obtained from dark-coloured acids.

Distillation was formerly accomplished by direct-firing of pot stills at about 300°C. (572°F.) accompanied by the introduction of superheated steam, the vaporized materials being condensed in air-cooled coils. The fatty acids obtained were considerably lighter in colour than the raw stock, but not very white as measured by present standards. A considerable percentage, varying from 10 to 20 per cent, depending on the character of the fatty acids, would remain in the still as a fatty acid pitch.

The present trend is toward vacuum distillation at about 100 mm. pressure of mercury, with superheated steam and temperatures of about 250°C. (442°F.) or even lower if higher vacuums are obtainable. Furnaces are carefully designed to minimize local overheating and under these conditions practically colourless products are obtained and the extent of pitch formation is reduced. However, there may still be considerable loss due to polymerization of the highly unsaturated acids such as are present in fish oils. In such cases it is desirable to hydrogenate the oil to remove the highly unsaturated acids and reduce the loss by pitch formation.

The Wecker system consists of spraying water or other liquid into the oil and transferring the mixture into a distillation chamber where it is subjected to high vacuum and injection of superheated steam. The Tolman-Goranflo (U.S. patents 1,951,241; 1,998,997; 1,998,998) process consists essentially of a countercurrent principle where the oil is preheated in a heat exchanger by superheated steam, then allowed to fall through the distillation chamber counter to the flow of steam. Intimate contact of the oil is obtained by means of screen trays or bubble-cap towers, and the distillation chamber is maintained under moderate vacuum.

The fatty acids thus produced are cooled under controlled conditions to secure the proper crystal size for separating the liquid and solid fractions and are pressed at 6° to 10°C. (43° to 50°F.) to separate the olein from the stearine. If a higher melting product is required the pressed cake may be melted, cooled and re-pressed at about 35°C. (95°F.), the solid "stearic" acid being designated "double pressed". Occasionally a third pressing at 55°C. (131°F.) is applied to obtain the special high-melting "triple pressed" stearic acid.

The stearine pitch produced is frequently known by the name of the oil or fat from which the acids were obtained, for example Linseed Oil Pitch, or Cottonseed Oil Pitch. It is formed partly by polymerization of the unsaturated fatty acids and partly by the decomposition of the unsaponified fats left in the charge.

Kronstein (see Lewkowitsch and Warburton, 1923, III, p. 131) distilled oils *in vacuo* and found that a certain amount of fatty acid distilled during the polymerization. Brocklesby and Denstedt (1934) showed that with pilchard oil the decomposition was very extensive by this process owing to the high temperature required, but, if the oil was first polymerized in the absence of air, and then subjected to steam distillation, partial hydrolysis took place and some fatty acids and other decomposition products were distilled.

It was subsequently shown that, if the oil was heated to 350° C. (662° F.) for one hour before distillation was begun, loss of unsaturated acids was reduced to a minimum, while the solid fatty acid content of the oil was decreased by 50 per cent. The distillation was continued until the oil suddenly thickened to a gel indicating extensive polymerization.

TABLE XLVI. Analytical data of distillates from steam-distilled oil

Sample	Time of steaming (min.)	Temp. (° C.)	Wt. (%)	Iodine value	Acid value	Solid f.a. (%)	Sapon. equiv. solid f.a.
1	15	360	11.8	90.1	195.1	27.3	251
2	30	350	5.4	72.5	222.1		
3	45	340	3.9	60.7	227.5	35.1	245
4	60	325	2.3	64.4	219.3		
5	75	310	1.6	61.5	191.7	35.9	256
6	90	308	1.1	59.4			
7	105	327	1.5	60.5		35.0	255
8	120	315	1.2	65.7			
9	135	317	1.1	55.6	196.2	35.7	243
10	150	319	1.3	62.9	187.0		
11	165	315	0.8	58.1	189.1	34.7	257
12	180	320	1.3	61.8	185.8		
13	195	325	0.8	....	179.2	33.4	258

Table XLVI shows the analytical data for distillates obtained during a typical run with pilchard oil. The oil was heated to 360° C. (680° F.) during one hour, after which time steam at a boiler pressure of 25 pounds was blown through the oil, which was maintained at approximately 320° C. (608° F.), the distillates being collected every fifteen minutes. The variation of acid and iodine values indicates considerable decomposition during the process, but no highly unsaturated acids distilled over. After the first fifteen minutes the solid fatty acid content of the distillate remained practically constant and from the saponification equivalent it appears that the solid components consisted mainly of palmitic acid. The first sample was the largest and contained most of the decomposition products of the preliminary heating period. The subsequent fractions decreased in size until after ninety minutes they became practically constant at 1 per cent. A further discussion of this process will be found in Section 5 I (*d*) (polymerization).

In recent years it has become possible to maintain pressures down to 10^{-2} to 10^{-6} mm. of mercury in relatively large pieces of equipment. At these pressures the mean free path of the molecules becomes relatively large and vaporization of even such non-volatile substances as the glycerides of long-chain fatty acids becomes a possibility at reasonable temperatures. Under these conditions, if a

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condensing surface is placed within the distance of the mean free path of the molecules from the heating surface, distillation may be accomplished.

This molecular or "short-path" distillation as it is variously called has been applied to fatty-acid distillation, distillation of glycerides, concentration of vitamins, removal of non-polymerized fractions and fatty acids from stand-oils by Imperial Chemical Industries and by Hickmann. (See also Brit. patents 428,-719; 452,442; 457,120; 457,292; 458,117; and U. S. pat. 2,073,327).

Essentially the process consists of passing the material to be distilled through a short heating zone in a thin film with the condensing surface within 1 to 5 cm. of the surface of the film. The whole apparatus is maintained at a pressure of 10^{-2} to 10^{-6} mm. of mercury. By this means the material is subjected to the higher temperatures required for distillation for a short time only, thus reducing polymerization and decomposition to a minimum. The flow of the film constantly changes the surface, preventing it from being impoverished of the lighter fractions.

There are two methods by which this process is carried out. In the first the inner of two concentric tubes is heated and the liquid is made to flow over it in a thin film. The outer tube is placed so that its inner surface is only 1 to 5 cm. removed from the outer surface of the inner tube. The outer tube is cooled and acts as a condenser (Hickmann 1937; and British patent 457,120). In the second method the lower of two moving belts passes over a heated zone, and the other runs parallel to it within a distance of 1 to 5 cm. and is cooled to act as a condenser. Suitable means are provided for removing the residue and the distillate, and for feeding the distillant uniformly in a thin film on to the lower belt. In each type the whole apparatus is enclosed and maintained at the desired low pressure.

By the use of these methods, vitamins may be concentrated to a considerable extent (Hickmann et al 1937, 1938), odourless vitamin-free oils may be obtained and cholesterol distilled. While this process is essentially in the experimental stage at present, it is rapidly becoming of industrial importance.

(h) Preparation of Vitamin Concentrates

The preparation of concentrates of vitamins A and D from fish body, liver and intestinal oils has assumed considerable importance during the last few years. The advantage of such concentrates for both human and animal use lies chiefly in the smaller doses required with consequent ease of administration. In addition, the removal of the organoleptically unpleasant oil allows such concentrates to be used for fortifying the vitamin content of many foods without detriment to their flavour. The manufacture of vitamin concentrates was at one time undertaken entirely by manufacturing pharmacists, but recently also those firms interested in the production of animal feeds have been producing concentrates for fortifying the vitamin content of poultry and animal feeding oils.

A complete review of the literature dealing with methods for the preparation of vitamin concentrates from fish oils does not fall within the scope of this Bulletin. The following survey is intended to show the trend in processing and to give a few examples of patented methods suggested for the preparation of such concentrates.

Methods for the concentration of the fat-soluble vitamins may be divided into three broad groups: (1) the oil is washed with a solvent which exerts a

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greater solvent action on the unsaponifiable matter than on the oil itself, (2) the oil is partially or wholly saponified, the unsaponified oil and/or unsaponifiable matter being removed by means of solvents, and (3) the vitamins are removed from the oil by physical means such as high vacuum "short-path" distillation or by adsorption on activated material.

(i) BY DIFFERENTIAL SOLUBILITY

This type of process is exemplified by two broad patents issued over ten years ago. United States patent 1,629,074 describes the use of glacial acetic or other organic acids to remove the vitamin fraction from cod liver or other vitamin-containing oil. In the example cited, cod liver oil is refluxed with an equal weight of glacial acetic acid for a period of 8 hours. The extracted oil is separated from the acetic acid extract and discarded. The extract is concentrated to about one-third of its volume during which time some oil separates out. This oil is also discarded and the concentration continued until the extract has but one-tenth its original volume. This residue is now taken up in a fat solvent and washed with water until free from acetic acid. The solvent is now evaporated off and the residue saponified with alcoholic potassium or sodium hydroxide. The soap solution is now extracted with a fat solvent and the unsaponifiable matter isolated. It is claimed that of all the solvents tried (formic acid, ether, ligroin, benzol, acetone, alcohol, ethyl acetate, etc.) acetic acid gave the most complete removal of the vitamins, and it is suggested that the acid hydrolyzes the vitamin fraction from the oil, thus facilitating its removal.

In 1928 Zucker obtained a patent (U.S. 1,678,454) containing 19 claims which cover the "process for the extraction of the antirachitic principles of cod liver oil." Of these claims the most interesting are: the use of alcohol to remove the active principle from the unsaponified oil, and the precipitation of the saponified fatty acids with calcium salts with removal of the active principle from the calcium soaps by means of solvents. These two steps may be used together as indicated in the following preferred example. Twenty gallons of cod liver oil is agitated during 2 hours with 10 gallons of 95 per cent alcohol. After settling, the upper layer of alcohol is siphoned off and the process repeated with 3 lots each of 5 gallons of alcohol. The combined alcoholic extracts are evaporated down to about 500 ml. and added to an equal amount of 40 per cent aqueous sodium hydroxide solution. After saponification is complete, the sodium soaps are put into solution by the addition of about 10 litres of water and a concentrated solution of calcium chloride added until precipitation of the calcium soaps is complete. An excess of calcium chloride is to be avoided and the solution must remain alkaline. The precipitated calcium soaps are filtered off and the adsorbed active material washed out of the soaps by repeated treatment with acetone. The acetone extract is evaporated down to 400 ml. and treated with 500 ml. of ethyl ether which dissolves the active principle. This ether solution is then washed with dilute alkali to remove any traces of soaps or fatty acids and then, when neutral, it is washed with dilute hydrochloric acid to remove any amines or other organic bases. Finally, the ether solution is washed neutral with water, dried with sodium sulphate and the ether removed by distillation.

It is to be noted that this patent also includes the extraction of the antirachitic principle from an oil by saponifying the oil with an alkali, extracting the mixture with ether and separating the antirachitic principle from the ethereal extract.

(ii) BY SAPONIFICATION

Methods involving the partial or complete saponification of the vitamin-rich oil are very numerous, and these may roughly be divided into the following groups: partial saponification, complete saponification with resultant soaps put into dilute solution with water or other solvents, complete saponification with resultant soaps produced in the anhydrous condition and complete saponification

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with resultant soluble soaps precipitated as water-insoluble soaps. A few patents will be described under these headings and in each case the particular novel feature of the patent will be indicated.

Partial saponification is used according to U.S. patent 1,753,790 to prepare a concentrated cod liver oil. Enough caustic soda or milk of lime is used to bring about from 50 to 75 per cent saponification of the oil. The unsaponified portion of the oil, which dissolves the unsaponifiable matter originally associated with the saponified portion, is separated by centrifuging or other suitable means. U.S. patent 2,026,395 describes a similar method, but in this case the soaps formed during partial saponification are dissolved in an "organic solvent or solvents which in conjunction with each other have the power of dissolving the water soluble soaps so as to form solutions of relatively low viscosity". The use of such solvents is also claimed to reduce the hydrolysis of the soaps and the separation of the vitamin-enriched unsaponified portion of the oil is therefore facilitated. According to both of these patents, the concentration of the vitamins of the original oil can be carried out to a predetermined extent by controlling the amount of saponification.

Dilute solutions of soaps, formed by the complete saponification of vitamin-bearing oils, are extracted by a variety of solvents to obtain a vitamin-rich concentrate. According to U.S. patent 1,786,095, the oil to be saponified is dissolved in a solvent that will also dissolve the vitamins, and saponified with alcoholic potassium or sodium hydroxide; the solvent containing the vitamins is removed from the precipitated soaps. As an example, 100 parts of the raw oil are treated with 200 parts of a 20 per cent alcoholic potash or soda solution and 200 parts of ethyl ether, and the mixture is allowed to stand for 24 hours at room temperature during which time complete saponification takes place. Two hundred parts of a 25 per cent alcoholic solution of calcium chloride are then added and the precipitated calcium soaps removed by filtration. The vitamins are recovered from the alcohol-ether mixture. Aqueous barium chloride may replace the alcoholic calcium chloride solution. The use of an edible oil as solvent for the extraction of the unsaponifiable matter from saponified oils is covered by U.S. patent 1,805,593. For instance, 100 parts of a fish liver oil are agitated with 360 parts of 5 per cent alcoholic potassium hydroxide until saponification is complete. Two hundred parts of sunflower oil are then added and thoroughly mixed with the saponified liver oil mixture. The emulsion is allowed to break and the sunflower oil is separated from the solution. The oil, now containing the unsaponifiable matter from the liver oil, will also contain some alcohol and it may be purified by vacuum distillation or by steaming. This patent also covers the extraction of vitamins and/or unsaponifiable matter by means of an edible oil from any *alcoholic* solution of alkali metal soaps.

In U.S. patent 1,947,315, a method is claimed whereby the saponification of the vitamin oil is effected by an aqueous solution of alkali hydroxide in the presence of a non-saponifiable and water-insoluble solvent which dissolves out the vitamins. As an example of this method 100 volumes of liver oil are dissolved in 25 volumes of a solvent such as pentane, and the oil is then saponified with sufficient aqueous potassium or sodium hydroxide with the aid of heat. The pentane solution is separated from the aqueous soap solution and the concentrate recovered by distillation of the solvent. The use of inert atmospheres to prevent oxidation of the vitamins during processing is stressed in this patent. U.S. patent 1,984,858 seeks to avoid the difficulties encountered when dilute soap solutions are extracted with solvents, and due to absorption of the oil by the soap and to the formation of persistent emulsions. According to this patent these difficulties may be overcome by suitable preparation of the saponified oil and by a well-designed continuous-extraction apparatus. An example of the preparation of the soap solution is given as follows: 400 gallons of liver oil is heated to 40° C. with 331 gallons of 61 per cent (by volume) alcohol. One hundred and nineteen gallons of caustic soda solution (containing 476 pounds of sodium hydroxide) is then added, and stirring and heating continued at 70° C. for 30 minutes when saponification will be complete. The soap solution is then cooled to 50° C. and 1,042 gallons of 25 per cent alcohol added. After complete mixing, sufficient ethylene dichloride is added to raise the specific gravity of the mixture to 1.024 at 70° C., the soap solution taking up

in the present example about 25 per cent of its volume of ethylene dichloride. This prepared soap solution is now extracted with pure ethylene dichloride in a continuous counter-current extractor, the fresh solvent entering the top of the extractor and the soap solution at a point slightly above the bottom. Owing to differences in specific gravity and to the physical characteristics of the soap solution quick and continuous separation of the two phases is obtained with no emulsification trouble. The vitamin-containing unsaponifiable material can thus be washed out of the soap solution quickly and efficiently.

The extraction of anhydrous or concentrated soaps is illustrated by the following typical examples. In U.S. patent 1,690,091 it is claimed that the difficulties inherent in the extraction of large volumes of dilute soap solutions can be overcome by saponifying the oil with an excess (10 to 15 per cent) of aqueous alcoholic potash. After saponification is complete the alcohol content of the solution is adjusted so that 60 grams of 30 per cent aqueous alcohol is present for each 100 grams of oil saponified. The result is a viscous-solid soap mass. This mass is then agitated with ethylene dichloride, using a volume about twice that of the oil saponified. The solvent is removed from the bottom of the container and several subsequent extractions made with the same solvent. The ethylene dichloride extracts are combined, dried with sodium sulphate and the solvent removed by vacuum distillation.

Extraction of solid anhydrous soaps is described in U.S. patent 1,715,945. As an example of this 1.4 kilograms of caustic lime is slaked with water somewhat in excess of the theoretical quantity, 10 kilograms of liver oil is heated in an inert atmosphere to 80° to 100° C. and the slaked lime introduced in small portions with constant stirring. The mass is allowed to stand for 18 to 20 hours, after which the solid calcium soaps are ground to a powder and digested with an edible oil such as cottonseed oil at 40° to 50° C. during 20 to 24 hours. After cooling, the oil is separated from the calcium soaps by filtration.

Solid anhydrous soaps are extracted by a method described in U.S. patent 1,879,734 that consists essentially in dissolving the fat or oil in a solvent in which soaps are insoluble, acetone being the preferred material. For instance, 100 grams of cod liver oil is dissolved in 700 ml. of acetone to which is added 15 ml. of water containing 25 grams of sodium hydroxide. The mixture is thoroughly stirred at room temperature for about 5 hours, after which the precipitated soap is filtered off and extracted with fresh acetone. The acetone extracts are combined and the solvent removed in a vacuum. A somewhat similar method is described in U.S. patent 1,919,369, and consists essentially in saponifying the oil or fat with alcoholic concentrated sodium hydroxide solution and adding to the saponified mass, which then contains less than one-fourth by weight of water, a "vitamin-solvent-soap-precipitant" consisting of either ether, dichlorethylether or acetone. The soap mixture is preferably hot when the precipitating solvent is added. If acetone is used, the excess of alkali in the saponified material is removed by treatment with sodium bicarbonate, in order to avoid polymerization of the acetone that occurs in the presence of alkali. The various steps of the process are carried out preferably in the absence of oxygen.

Extraction of precipitated water-insoluble soaps is the subject of U.S. patent 1,897,039, wherein water-soluble soaps resulting from the saponification of an oil are precipitated by means of a soluble aluminium salt. In order to avoid the formation of basic soaps and the hydrolysis of the aluminium soaps, alternate neutralization and reprecipitation are necessary as shown by the following example: 100 grams of cod liver oil is dissolved in 800 ml. of alcohol and saponified by the addition of 40 grams of potassium hydroxide. To the boiling saponified solution is added 245 ml. of a 20 per cent alcoholic solution of aluminium chloride and boiling continued for half an hour. The reaction mixture is then alternately neutralized with 4-normal potassium hydroxide solution and aluminium chloride solution in the following amounts: 12.7 and 20.0 ml.; 5.3 and 8.4 ml.; 2.7 and 4.2 ml.; and finally, 2.0 and 4.0 ml. Whilst still hot, the precipitate is filtered off and treated with 200 ml. of boiling alcohol; the alcohol extracts are combined and neutralized with alcoholic potassium hydroxide and reprecipitated with aluminium chloride until no further precipitation is visible. The precipitate is filtered off and the filtrate evaporated to dryness. The residue may be taken up in a small quantity of edible fat or oil.

(iii) BY VACUUM DISTILLATION

Within the past few years the application of the so-called "molecular" or "short-path" vacuum distillation methods to the isolation of vitamin concentrates has proven to be of outstanding interest. An outline of the apparatus used is given in Section 8 II (g) of this Bulletin. There are several ways in which this method may be applied to the concentration of vitamins. U.S. patent 1,925,559 describes how a cod liver oil may be subjected to "vacuum extraction" when a small amount of an oily fraction containing the vitamins sublimes and is condensed on the cold surface of the still. This fraction still contains some oil, and some vitamin is left in the main body of the oil. To obtain a greater control over the process Brit. patent 482,881 describes how oils, containing only small amounts of vitamins, are admixed with a synthetic mixture compounded so as to give a constant or known amount of distillate with each increase in temperature, each fraction containing a certain proportion of the vitamins. Brit. patent 487,367 covers the purification of the distillate obtained by the vacuum treatment of fish oils in which the distillate is one-third saponified and the unsaponified fraction removed and again subjected to vacuum distillation. According to this patent when the initial oil is vacuum-distilled, the fraction that contains the high-boiling ester-forms of vitamins A and D may be used directly for therapeutic purposes, whilst the fractions coming over before and after the above-mentioned fraction may be purified in the manner suggested. U.S. patent 2,146,894 protects the process that involves the addition to the oil to be distilled of such substances as distil at the boiling point of the vitamin to be removed. This means that vitamins may be removed in fractions of predetermined composition.

In order to obtain vitamin-rich fractions that may be added directly to foodstuffs such as margarine, a method described in Brit. patent 452,442 employs high-pressure hydrogenation either before or after vacuum distillation to yield an odourless and tasteless concentrate high in vitamin content. As an example, cod liver oil is hardened by treatment with hydrogen at a temperature not exceeding 60° to 70°C. and a pressure of 120 atmospheres in the presence of 2 to 3 per cent of finely-divided nickel supported on kieselguhr to give a paste-like mass of fairly hard consistency at room temperature. The sample loses not more than about 10 per cent of its vitamin A potency during the operation. The hardened material is then subjected to vacuum distillation at a pressure of 10^{-3} mm. Hg. and a temperature of 180°C. The condensate, about 8 per cent of the volume treated, is odourless and tasteless and contains about 7 to 8 times the vitamin potency of the original oil.

The adsorption of vitamins on activated solids such as alumina, silica, calcium carbonate and the like has been employed extensively in laboratory processes for the isolation of vitamins A and D, but up to the present, in spite of extensive investigation, no method has been devised for the commercial concentration of vitamins by this means.

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SECTION 9. INDUSTRIAL UTILIZATION OF MARINE ANIMAL OILS

The extent and diversity of the industrial utilization of marine animal oils are to-day largely a matter of economics. With the development of modern processing methods it is now possible to convert marine animal oils into a variety of products suitable as raw materials for a large number of industries. In the following pages some actual and suggested uses of these oils are given. The great range of these uses immediately becomes apparent and, while some of the writers of this Section have had considerable experience in certain of the industries mentioned, we cannot claim to have had actual experience in all of them. In those industries where the nature of raw materials can be described accurately in chemical and physical terms it is possible to state definitely whether or not a particular marine animal oil or a derivative can be produced to meet the specified requirements. On the other hand, where the selection or use of raw materials by any particular industry is still more or less of an art, the application of marine animal oils can be justified only after considerable experiment by those actually engaged in the industry. For this application the writers have tried to get first-hand information from the particular industries concerned, either by personal visits or by co-operative investigations. Most users of vegetable and animal fats and oils in Canada have been consulted and their opinions and suggestions incorporated in the text.

I. USAGE ACCORDING TO INDUSTRIES

(a) HUMAN FOODS.

The utilization of fats and oils by the animal body is treated in detail in Section 4 and it is sufficient to emphasize here the fact that these materials have a calorific value of about 9.3 calories per gram, as compared with 4.0 for carbohydrates. Thus fats and oils are important in the diet because of their high energy value.

Hydrogenated fats have nutritive values equal, if not slightly superior, to those of normal untreated fats. The ease of digestion, however, is apparently inversely proportional to the melting point; thus short-chain fatty acids and the unsaturated fatty acids are more readily absorbed than the acids with higher melting- point. The important factor is the ease of emulsification of the fat, those melting below 40°C. being much more readily emulsified in the intestinal tract than those of higher melting point.

The rate of hydrolysis of the fats is directly related, not to the iodine value, but to the melting point; hence the iodine value is of importance only as it relates to the melting point. However, the relationship of melting point to ease of digestion does not always appear to be a simple one. Hartwell (1939) has exam-

ined the rate of digestion of a number of fats and hydrogenated margarines by digestion *in vitro* with a pancreatic extract. Olive oil digests more slowly than butter fat but at a rate comparable with beef, mutton and bacon fats. Different brands of margarines digested at different rates; some were rapidly digested and gave results equal to those obtained with butter fat. On the other hand some margarines were digested slowly but even these gave faster rates than that of olive oil. The reasons for the unequal rates of digestion of the hydrogenated margarines have not yet been fully elucidated.

The iso-acids formed during the hydrogenation of fats are as easily absorbed as the naturally-occurring acids of similar melting points, and synthetic lard prepared by re-esterifying the fatty acids of lard with glycerol is as easily digested as the original lard.

(i) SHORTENINGS

These are fatty materials used in baking pastry and similar products to give a flaky and crisp effect in the finished article. Originally lard was used exclusively, but modern shortenings consist mainly of hydrogenated fats. Chiefly vegetable oils are used, but a considerable amount of whale oil is combined in certain grades of shortening. The oils are usually hydrogenated to a melting point of about 30°C. (86°F.), and then, after thorough mixing, are chilled and kneaded until the product has the appearance of lard.

Frequently it is found that a better product is obtained if a blend of oils is used, where one portion is hydrogenated to a melting point of about 40°C. (104°F.), while the other is hardened to a melting point of only about 25°C. (77°F.). In many cases, untreated oil is blended with more or less hardened fat depending upon the characteristics required. The main undesirable feature in using unhydrogenated oil is the possibility of rancidity occurring owing to the presence of some of the more unsaturated acids.

Measurement of the shortening quality is best made by baking tests, but the efficiency of these products is known to depend on the emulsifying properties which are determined by the melting point and the consistency. These two properties are usually closely related in individual fats but may vary widely in blended shortenings. Thus shortenings that have the same melting point may vary from firm fats to those of soft consistency.

By emulsifying power of a fat is meant its power to form an emulsion with water, milk, air, etc., when beaten together. Certain fats when beaten with eggs, sugar, milk, etc., will hold enough air to increase the volume 70 per cent. This is known as the "creaming power", and is the property responsible for the proper distribution of the fat throughout the baked product, with consequent effect upon lightness and texture.

(ii) COOKING FATS

The main essential in cooking and frying fats is a high smoking or decomposition temperature. During decomposition volatile irritating products are formed and fatty acids of low molecular weight accumulate in the fat. Natural

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fats all have low smoking temperatures and are not very suitable for use in frying, but, when they are hydrogenated, the smoking temperature is raised very materially, e.g. lard has a smoking temperature of 188° to 204°C. (370° to 400°F.) while hydrogenated oils range up to 260°C. (500°F.) depending upon the extent of hardening.

Using hardened oils, higher cooking temperatures may be used with more rapid searing of the surface of the material, thus securing better retention of the natural juices and less penetration of the cooking fat into the product.

(iii) MARGARINE

This is the name given to the various types of butter substitutes. Since many different vegetable and animal oils are used in the preparation of this type of product, the composition will vary widely. Natural oils may be used but hydrogenated oils are being more and more extensively used in various parts of the world. Whale oil is finding increasing application in Europe, and other marine animal oils will probably find more extensive use in the future.

Usually the mixture of oils or fats is blended to secure a product that melts at 22° to 27°C. (72° to 81°F.), varying slightly with the season of the year. For table use the fats are melted and churned with milk that has been sterilized by pasteurization, then inoculated with lactic acid bacteria, and "ripened" to the desired acidity and flavour. The liquid emulsion from the churning is then solidified by chilling, kneaded to remove the excess liquid, salted, coloured, and plodded to produce a product that sometimes can only with difficulty be distinguished from butter.

(b) CLINICAL USE.

It is now well established that vitamin A is necessary for growth, vision and normal functioning of certain specialized tissues of the body. Its growth-promoting action was the first to be recognized and although probably a secondary effect, resulting from bodily misfunctions, the rate of growth is none the less related to the intake of vitamin A.

A deficiency of vitamin A has two apparently separate effects on vision, both of which are found in cases of relatively mild deficiency. One of these effects is night blindness and the other is an infection of the cornea, called xerophthalmia. The present knowledge of night blindness is almost entirely derived from the work of Wald at Harvard University. He has shown that vitamin A itself forms part of the molecule of a pigment, visual purple, which is necessary for the transmission of stimuli to the optic nerve when light falls on the retina. Visual purple is broken down by light, ultimately to vitamin A. Although the pigment is re-synthesized, there is some loss of vitamin A in the process, so that more must be continually supplied.

Vitamin A is essential for the proper functioning of certain tissues. Its chief function in this respect is the maintenance of the epithelial tissues of the body in normal condition. In cases of vitamin A deficiency the skin becomes abnormally

dry and scaly. Many local infections, such as colds and other infections of the respiratory tract, may be traced to the greater ease with which bacteria can attack the surfaces when such a condition prevails.

Degenerative changes in the structure of teeth and nerves have been associated with the advanced stages of vitamin A deficiency in man. Kidney stones have also been found under the latter conditions. It has not been proven, however, that these disturbances are due to a lack of vitamin A.

Vitamin A has frequently been called the "anti-infective" vitamin, since a liberal supply of it in the diet reduces susceptibility to respiratory and other infections. It is now generally agreed, however, that vitamin A has no specific anti-infective action. The latter is a secondary effect. When an individual is suffering from vitamin A deficiency, the resulting dry, scaly condition of the epithelia, which has already been mentioned, markedly increases the ease with which the membranes are attacked by bacteria. It has further been proven, within recent years, that an animal deprived of vitamin A does not lose its power to form the "antibodies" by which it resists the attack of disease-producing agents entering the blood stream.

A considerable number of papers has been published in the medical journals dealing with the subject of the curative action of vitamin A-containing oils when applied externally to wounds. In practically all cases favourable results have been reported. For example, Sandor (1936) found that wounds healed more rapidly when a solution of vitamin A in petrolatum, containing 2000 International units of the vitamin per c. c., was applied, than with the application of the petrolatum alone. It is somewhat difficult to suggest a reason for this, particularly since vitamin A has no direct anti-infective action, but it is probably related in some way to the building up of an increased local reserve of the vitamin. It has been demonstrated by Helmer and Jansen (1937) that vitamin A is absorbed through the skin when a potent halibut liver oil is applied externally.

Until recently little was known regarding the actual amounts of vitamin A required by man, and it has been common clinical practice to ensure an adequate supply by the administration of quantities which were known from experience to be more than sufficient. The actual human requirements have, however, been the subject of considerable study during the past few years. The American Public Health Association Committee on Nutritional Problems (1934-1935) recommended an intake of 1,500 International units per day for infants. Jeans and Stearns (1938) advocated 300 to 400 units per day for children from birth to adolescence. Booher, Callison and Hewston (1939) found, in an experimental study, that the daily vitamin A intake necessary for the prevention of night blindness in normal adults varied in the five subjects studied, from 25 to 55 International units per kilogram of body weight.

The abnormalities which result from a deficiency of vitamin D in human nutrition are confined almost entirely to the bones and teeth. Rickets and osteomalacia, which have already been described in an earlier section of this Bulletin, are the most prominent disorders. The abnormal structures and poor

calcification, which are the commonest results, can be corrected by an adequate dietary supply of calcium, phosphorus and vitamin D.

Failure of fractured bones to re-unite has been ascribed to lack of vitamin D. Although favourable results have sometimes been obtained in such cases by administration of vitamin D, there is not sufficient evidence to show whether the vitamin alone was responsible.

Severe vitamin D deficiency in children leads to nutritional tetany, one variety of "convulsions". The immediate cause of the disorder is low blood calcium, which in turn may be due to insufficient vitamin D. Nutritional tetany can be cured or prevented by administration of this vitamin.

The human requirement for vitamin D, unlike that for vitamin A, is greatest in infancy, and decreases as adulthood is approached. The American Public Health Association Committee on Nutritional Problems (1934-1935) has stated that the minimal daily dose of vitamin D which will protect an infant from rickets is 700 International units, but that the requirement is considerably less after the first two years of life. The amount of vitamin D necessary for man is undoubtedly dependent on the amounts of calcium and phosphorus in the diet, as it is in the case of other animals. The relationship in this case has not been studied very extensively, and would certainly warrant further investigation.

Although cod liver oil was for many years the common medicinal source of vitamins A and D, during the past decade various other oils have been introduced. Halibut liver oil was the first of these. Its potency in both vitamins, but particularly in vitamin A, is much higher than that of cod liver oil. Thus the amount of oil which must be taken in order to secure the same amount of vitamin is much lower for halibut than for cod liver oil. This enables individuals who are physically unable to tolerate cod liver oil, or who find the necessarily large dose of the latter nauseating, to obtain an adequate supply of vitamins A and D. Plain halibut liver oils are available standardized at potencies ranging from 10,000 to 50,000 International units of vitamin A per g., and 250 to 900 International units of vitamin D per g.

The liver oil from fishes of the percomorph group, which includes the tunas, is a potent source of vitamin D but relatively low in vitamin A. Although the natural unblended oil was placed on the market for a time, it was never very widely used on account of the low vitamin A potency. Percomorph liver oil is now blended with halibut liver oil, cod liver oil or cod liver oil concentrates to secure a better balance between the two vitamins present.

Halibut and cod liver oils are also blended with the artificial vitamin D produced by the activation of ergosterol or cholesterol. Such blended oils are available with the vitamin D potency increased from two to forty times the original.

There is still a considerable demand for cod liver oil. Many different grades of this oil are now sold. Some are biologically standardized, but others are merely stated to be of "highest quality" with no guarantee of potency. The minimal requirements for vitamins A and D set by the United States Pharmacopoeia (600 International units of vitamin A and 85 International units of vitamin D per

gram) are frequently used as a basis for describing tested oils. Thus cod liver oils are often specified as containing vitamins A and D "in excess of pharmacopoeia requirements". Some natural cod liver oils are sold with claimed potencies as high as 4500 International units of vitamin A and 500 International units of vitamin D per gram, but the average claimed for standardized oils is more commonly about 2500 units of vitamin A and 250 of vitamin D per gram. Unstandardized cod liver oils probably fall considerably below these potencies.

Many specially prepared concentrates of vitamins A and D from fish oils are available on the market. While the vitamin potencies of such products are usually given on their labels, the oils from which they were prepared are often not stated. These preparations are usually sold in capsules. Plain and blended oils of high potency such as halibut liver oil are available both as the oil and in capsule form.

(c) ANIMAL FEEDING.

(i) POULTRY

It is only within fairly recent years that the necessity for vitamins in poultry feeding has become evident. The continual attempt of poultry producers to raise chicks earlier in the year has resulted in the young birds being grown at a time when there is little sunshine. Direct sunshine, by virtue of its ultraviolet rays, prevents rickets. Young chicks raised very early in the spring, particularly in the more northerly latitudes, do not get enough exposure to direct sunlight to prevent rickets, or leg-weakness as the chick disorder is called. Other means must, therefore, be taken to prevent it. The results which have been obtained in feeding cod liver oil to rachitic children led to its use in the prevention and cure of leg weakness in "early" chicks. Not only was the disorder overcome when a sufficient quantity of the oil was fed, but other beneficial results were observed. The birds generally grew faster and fewer died before reaching maturity. When the oil was fed to adult birds, still other advantages became apparent. These included increased egg production, increased hatchability of the eggs and better shells. It was also found that the vitamin content of the eggs was increased when the laying hens received a liberal supply of vitamins in their ration.

It was recognized that the value of cod liver oil in poultry feeding was due to its content of vitamins A and D. This led to the investigation of other less expensive oils which were known to contain these vitamins. Several were found to be comparable with cod liver oil in this respect. British Columbia pilchard oil, California sardine oil, menhaden oil and the oil produced from salmon cannery waste were among these.

For some time irradiated ergosterol was also used as an antirachitic for poultry. However, when Massengale and Nussmeier (1930) showed that the antirachitic value of this substance was comparatively far less for poultry than the vitamin D in fish liver oil, its general use was discontinued. Bethke, Record, Kick and Kennard (1936) also showed that irradiated ergosterol was inefficient in promoting egg production and hatchability.

In many of the investigations on the use of vitamin-containing oils in poultry feeding, rations have been used which were purposely designed to have a low content of the vitamin being investigated. In other investigations regular farm rations have been used. Comparison of the results obtained with ordinary rations and with the specially prepared mixtures showed, among other things, that the amount of vitamin D necessary was very much lower when the ration contained approximately equal amounts of calcium and phosphorus, and contained both in adequate quantities. This phenomenon, which has already been discussed in an earlier section of this Bulletin, is very marked in the case of chickens. Carver, Robertson, Brazie, Johnson and St. John (1934) state that growing pullets, when in confinement without sunshine, required from the first to the 16th week of age a minimum of 17 International units of the vitamin D in cod liver oil per 100 grams of ration for satisfactory calcification and growth. From the 16th to the 24th week of age the requirements were 8 units per 100 grams of ration. Egg production was seriously reduced by insufficient vitamin D in the ration. For satisfactory egg production and egg quality from hens in confinement without sunshine, 67 units of the vitamin D in cod liver oil per 100 grams of ration were required. For satisfactory hatchability of eggs from hens in confinement without sunshine, 135 units of the vitamin D in cod liver oil per 100 grams of ration were necessary. It was found necessary to supplement the direct sunshine of winter with 34 units of vitamin D for satisfactory hatchability of eggs. The Poultry Husbandry Department of the Ontario Agricultural College recommend 100 units of vitamin D per 100 grams of ration for satisfactory egg production and hatchability.

Biely and Chalmers (1936) concluded from their experiments that 75 International units of vitamin A per day would ensure normal growth and protect chicks against any symptoms of vitamin A deficiency up to 8 weeks of age. Tepper and Durgin (1938) found that the vitamin A requirements of growing chicks increased as they approached maturity.

Gutteridge (1932) showed that, under conditions closely similar to those found in the average poultry farm, pilchard oil was as efficient as cod liver oil in supplying vitamin D to growing chicks. The data obtained for the bone ash, which was used as a criterion in evaluating the vitamin D, were as follows:

Supplement	Ash content of tibia-fibulae, taking highest percentage as 100
None	55.6
1% pilchard oil no. 2	100.0
1% cod liver oil	97.8
2% pilchard oil no. 1	80.8
2% pilchard oil no. 2	93.3
2% cod liver oil	97.6
Direct sunlight	93.0

In a subsequent study the same author (1933), using a ration deficient in vitamin A, found that pilchard oil and cod liver oil were of equal value as sources of vitamin A for poultry.

Carver and co-workers (1933) found that, while the addition of 0.5 per cent of either British Columbia pilchard oil or California sardine oil to a ration deficient in vitamin D caused some improvement in the bone formation and the growth of young White Leghorn chicks, it was not sufficient to bring about normal function. Tepper and Reed (1935) made a comparative study of sardine oil and cod liver oil for chicks. They concluded that sardine oil was as efficacious as cod liver oil in supplying the young birds with vitamin A.

Menhaden oil has also been used as a vitamin supplement in poultry feeding. Supplee (1937) found that the bone ash of young chicks fed a basal ration supplemented with 1/8 and 1/4 per cent menhaden oil, was comparable to that ordinarily produced by similar amounts of cod liver oil.

The oil produced from salmon cannery waste contains both vitamins A and D. Davis and Beach (1926) fed 1 cc. of salmon oil per day, supplementing a basal ration deficient in vitamin A, to a group of 10 pullets. A similar group of 10 pullets was given the basal ration only, with no supplement. The control group produced only 2 eggs during the experimental period and 6 of the birds died during the experiment. The survivors showed a gain in weight of 24.7 per cent. Only 1 of the birds in the salmon oil group died during the experiment. The survivors showed a gain in weight of 44.5 per cent and produced 29 eggs during the experimental period. The same authors subsequently (1928) investigated the antirachitic value of salmon oil for poultry. Fifty chicks, 3 days old, were divided into 2 groups of 25 each. The experiment was carried on for 3 months. All the birds fed salmon oil survived the experiment and none of them developed rickets. Two of those in the control group died, and only one of the survivors failed to develop rickets.

It is now recognized (Bills *et al.* 1937) that not only does the concentration of vitamin D vary widely in the liver oils of fish of different species but that the vitamin varies in kind. In other words, natural vitamin D is not one single substance but may be a mixture of different substances. Based on the unit antirachitic effect on rats, it has been found that there is considerable difference among the efficiencies of various fish oils when fed to poultry. Most of the work has been done with cod liver oil as the standard, feeding equal rat units of the cod liver oil and the oil under examination to growing chicks. The ash content of the femur of the chicks receiving cod liver oil is then compared with that of the chicks receiving the experimental oil, and taking the efficiency of the cod liver oil as 100, the relative efficiency of the experimental oil is estimated. With this method it has been found that the vitamin D in sardine (pilchard) body oil, halibut liver oil, ling cod liver oil and black sea-bass liver oil is equal in efficiency to that in cod liver oil; and that the vitamin D in the liver oil of the white sea-bass, black cod, dogfish, basking shark, swordfish and yellowfin tuna is more efficient than that in cod liver oil, while several of the tunas, notably the California bluefin, the albacore, striped tuna and California bonito have liver oils the vitamin D of which is definitely less effective on chickens than on rats. Remp and Marshall (1938) have reported that the minimal protective dose for chicks fed a rachitogenic diet was 2.5 units of cod liver oil, 2.5 units of crystalline vitamin D_3, 2.7 units of irra-

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diated cholesterol, 120 units of viosterol (irradiated ergosterol) and 85 units of crystalline vitamin D_2. In view of the fact that many mixed liver oils are now being offered to the poultry trade, and of the growing sale and use of vitamin "concentrates", it is essential that the vitamin D potencies of such substances should be stated in "chick units" and not in rat units. Where the genuineness of an oil is above question and where the rat-chick ratio is known, a rat assay may be used as a guide to the vitamin potency with respect to chicks, but even here caution must be used, as it is well known that the rat-chick ratios are not constant for any one oil and may vary almost as much as the actual vitamin D potency itself.

TABLE XLVII. Feeding oils used in mixed feeds in Canada during 1938-1939

Kind and grade of oil	Canada			Maritime provinces	Quebec	Ontario	Prairie provinces	British Columbia
	gal.	% of total oil	% of total vitamin D*	(gal.)	(gal.)	(gal.)	(gal.)	(gal.)
Cod liver oil								
Straight..............	38,048	13.5	5.6	2,555	8,775	20,646	4,582	1,490
100 D.1,000 A........	21,940	7.8	3.8	....	2,400	15,390	4,739	211
110 to 280 D. ⎱								
1,450 to 3,000 A ⎰	9,408	3.3	2.1	....	2,030	6,528	....	50
400 D.1,850 A........	49,589	17.6	34.3	2,025	4,855	41,014	250	1,445
400 D.3,000 to 3,500 A.	33,560	11.9	23.2	1,350	7,561	20,713	1,390	2,546
Total...........	152,545	54.1	69.0	5,930	25,621	104,291	10,961	5,742
Equal tons.......	686.45	....	....	26.69	115.29	469.31	49.32	25.84
Pilchard oil								
Straight..............	14,516	5.1	2.1	....	1,598	5,476	1,932	5,510
85 D.1,000 A........	10,964	3.9	1.6	....	......	10,964	....	....
100 D.800 A..........	78,821	28.0	13.7	....	6,904	24,758	24,183	22,976
200 D.1,200 to 1,500 A.	11,114	·3.9	3.8	....	1,059	8,745	376	934
400 D.1,850 A........	10,982	3.9	7.6	......	......	10,442	....	540
400 D.3,000 A........	3,147	1.1	2.2	......	534	1,913	450	250
Total...........	129,544	45.9	31.0	......	10,095	62,298	26,941	30,210
Equal tons.......	582.95	....	....	......	45.43	280.34	121.23	135.95
Grand total.......	282,089	100.0	100.0	5,930	35,716	166,589	37,902	35,952
Equal tons.......	1269.40	....	....	26.69	160.72	749.65	170.55	161.79

*"Straight" oil calculated as 850.

In table XLVII are given data showing the amounts and kinds of fish oils used in mixed feeds in Canada during 1938-1939. Of the total oil used 54 per cent was cod liver and 46 per cent pilchard. The amount of straight oil of either kind was, however, relatively small, being but 18.6 per cent of the total, the remainder being fortified or blended oils. The data show quite clearly the trend towards the use of fortified oils, particularly in the case of the cod liver oils, which, forming but 54 per cent of the total volume of the oils used, furnished 69 per cent of the total vitamin D.

Fish oils are not used as extensively in feeding farm mammals as in feeding poultry, since the ordinary feeds used for the former contain more of the required nutrients. They are, however, fed to some extent. During the winter months pigs frequently develop a rachitic condition which can be corrected by the administration of vitamin-containing fish oils. Fraser and Stothart (1934) showed that the growth of young pigs could be improved by feeding either pilchard oil or cod liver oil. They carried out an experiment in which three groups of young pigs, six in each, were kept under observation for 130 days. During that period all received the same basal ration. One group was given pilchard oil in addition and another group cod liver oil. The third group served as a control. Each of the oil-fed groups consumed altogether between 5 and 6 gallons of oil. The total gain in weight of the pilchard oil group during the experiment was 817 lb., of the cod liver oil group 844 lb. and of the controls 715 lb.

Some of the pigs were killed immediately after completion of the oil-feeding tests and the meat cooked at once. Others were fed for a subsequent period of 30 days without oil before they were killed and the meat submitted to the cooking test. The samples of meat from those slaughtered immediately after oil-feeding all had a fishy taste, but the meat from animals kept for 30 days without oil was entirely free from it.

As early as 1913 Hendrick showed that cod liver oil and skim milk could be used to replace whole milk in the feeding of calves. It is important to use the best quality of oil in feeding calves, since they appear to be particularly susceptible to the toxic materials found in inferior oils.

Mattick (1928) showed that the milk from cows which were fed 6 to 8 per cent cod liver oil daily supplementing a well-balanced ration had greater antirachitic properties than the milk from cows fed the same ration but supplemented with peanut oil instead of cod liver oil.

The alleged toxic factor in fish oils has been discussed in Section 4 of this Bulletin.

(iii) FUR-BEARING MAMMALS

Very few data are available regarding the use of vitamin-containing fish oils in the nutrition of fur-bearing mammals; La Beree (1938) states that the diet of minks should be supplemented with at least 25 units of vitamin A and 45 units of vitamin D from December 1 until the young produced the following spring are weaned. Bowness (1938) recommended that 1 per cent cod liver oil should be included in the diet of the breeders (both fox and mink) throughout the entire year, and that fox pups should be fed 1 tablespoonful to every 4 pups and mink half that amount, until August 1, when it may be omitted from the ration of all except those animals saved for breeding stock.

Fresh fish are used to a considerable extent in the feeding of fur-bearing mammals. When they are strictly fresh, it is customary to feed the entire fish, so that the animals will get the nutritional principles contained in the liver and

other visceral organs. It is common experience that when fresh fish are included in their diet the animals grow faster, keep in better condition and have superior fur. Since this is probably due, at least in part, to the vitamins of fish liver oil, it would appear that the use of fish oils in the nutrition of fur-bearing animals should be a fruitful field for investigation.

(d) Paints and Varnishes

Practically all fish oils will absorb oxygen on exposure to the air and, in the case of certain oils, notably menhaden, California sardine and Canadian pilchard, eventually dry to a solid film. The drying properties of these three fish oils in particular has led to their moderate use in paints and varnishes. Whilst it is recognized that protective coatings containing fish oil have certain desirable properties such as flexibility, there is much controversy in the literature of the subject and also in the opinions of paint and varnish manufacturers as to the general utility of fish oils. To a certain extent this controversy is a result of the lack of precise information regarding the properties of fish oils and their behaviour in paints and varnishes. The object of this part of the Bulletin is therefore to summarize and evaluate the published information on the subject, to present the views of a number of paint and varnish makers and, finally, to record some investigations made in these laboratories during the last few years by Dr. O. F. Denstedt and the writer. It is hoped that the data presented will enable the reader to judge of the relative utility of fish oils in paint and varnish manufacture.

(i) amount of fish oils used

Canadian paint and varnish manufacturers used 70,000 gallons of fish oil in 1935 and 111,000 gallons in 1936. The latter figures represent a consumption of about 3.8 per cent of the total oils used in this industry. The average cost at the plant was 47 cents per imperial gallon. Of the total quantity of fish oils produced in the United States (excluding whale oil) amounting to almost 100,000 tons in 1937, about 11.5 per cent was used in the paint and varnish industries, an amount approximating 2,500,000 imperial gallons. No statistics are available for the consumption of fish oil by the paint and varnish industries of Great Britain and Germany, but from the number of technical researches reported from the latter country, it may be assumed that the consumption is considerable. Japan has also evidenced considerable interest in the production of drying oils from Japanese sardine oil.

(ii) processed fish oils commercially available

Crude fish oils are rarely, if ever, used in the manufacture of paints and varnishes. Menhaden, sardine and pilchard oils all contain stearine which must be at least partially removed by refrigeration before use. In addition, bleached or decolorized oils are required for certain purposes as also are polymerized and blown oils. Many large paint and varnish manufacturers polymerize and blow their own oils, but there is an increasing tendency for oil refiners to supply such products made to definite specifications. The following list of processed fish oils is taken from the specifications of a reputable refiner in the United States. The products are derived entirely from crude sardine oil.

Oil No. 502

Crude oil filtered at atmospheric temperature to remove impurities and some stearine. Minimum iodine value 190, maximum acid value 3.0. This oil is used as a base for further refining. Sold as a heat resisting paint oil, linoleum oil, etc.

Oil No. 503

Same as no. 502 but bleached to a light colour.

Oil No. 532

Made from no. 502 by refrigeration and removal of stearine until product will stand cold test of 32°F. for three hours. Minimum iodine value 195. Fast kettling properties and extensively used in varnishes, enamels and paints.

Oil No. 532A

Same as no. 532 but bleached to a very light colour.

Oil No. 512B

Made from no. 532 but alkali refined and bleached. Maximum acid value 0.25. Colour 21 yellow and 2.5 red. Recommended as a standard oil for paint trade. Fast kettling with low losses giving very pale products with high gloss.

Oil No. 540

Made from no. 502. Unbleached but refrigerated to stand cold test of 40°F. for 3 hours. Minimum iodine value 192.

Oil No. 540A

Same as no. 540 but bleached to light colour.

Oils 522, EL, L, M and H

These four oils in the 522 series are heat bodied oils described as extra light, light, medium and heavy. Their specifications are as follows:

Oil	Iodine value	Sp. gravity at 25°C.	Acid value	Viscosity (G–H)
EL	125–130	0.955	2–3	R
L	120–125	0.960	2–3	U
M	118–120	0.965	2–3	W
H	115–120	0.970	2–3	Y
EH	110–115	0.975	3–4	Z

The colour of these bodied oils is 3 on the Gardner-Holt scale, the light colour and low acidity being in part due to the use of corrosion-resisting vessels during heat-bodying. The products are recommended for varnish, enamel and lithographic ink manufacture.

Heat-bodied sardine oils are also obtainable with driers added and a series of oils similar to the 522 series is available but of higher acidity and darker colour.

A series of air-blown sardine oils is produced with the following characteristics:

Oil	Iodine value	Sp. gravity at 25°C.	Acid value	Colour (G–H)	Viscosity (G–H)	
571–L	110–115	0.990	8–9	9	Z3 at 100°F.	light
571–M	100–110	1.015	9	9	Z5 "	medium
571–H	100–110	1.025	10	10	Z5–Z6 "	heavy
571–EH	100–105	1.027	10	10	Z6 plus "	extra heavy
596–EH	100–110	1.000	100–120	Dark	2×Z6 "	extra heavy

This 571 series of oils is supplied both uncut and cut. They are recommended for barn paints and for printing inks. The dark high-acid oil, 596–EH will dry to a tack-free film when compounded with ester gum. Alone, it will bake to a hard non-tacky film at 250°F. It is recommended for low-cost black enamels, cheap barn paints, asphalt paints, roofing compounds and insecticide sprays.

A similar variety of products is now made in Canada from Canadian pilchard oil. The availability of these processed oils, each one made to a definite specification, will no doubt stimulate the further use of fish oils in the protective-coating industries. In the past, although pilchard oil wintered to definite specifications was available to paint and varnish manufacturers, a considerable quantity of so-called "top oil" was marketed. The characteristics of these top oils, of course, varied with the temperature and with the time the oil was allowed to stand in the storage tanks, and it was practically impossible to furnish an oil of uniform quality. The result was that manufacturers who had experimented with sample shipments of pilchard oil and found certain uses for this oil in the formulation of their products could not duplicate the results on successive shipments. Purchase by rigid specifications will alleviate this trouble to a great extent.

(iii) REVIEW OF INVESTIGATIONS

Numerous reports on the use of fish oils in paints and varnishes have appeared during the last few years. As long ago as 1925, Toch, in his well-known book on the chemistry and technology of paints expressed the opinion that "results obtained from the proper grades of fish oil warrant the use of fish oil in the hands of an intelligent manufacturer. . . ." In 1936 this same author reported that sardine oils are superior to pilchard and herring oils for use in paints, but that all fish oils yellow more than other drying oils and that, when the humidity rises above normal, a fish oil paint becomes tacky for months afterwards. Kellam (1933) reports some work done on paints prepared with linseed, tung and pilchard oils and concludes that fish oils impart elasticity, blooming, non-yellowing and non-discolouring properties. Branke and Shavskii (1935) claim that when sardine oil, freed of the solid saturated stearine, is combined with 20 per cent by weight of resin, heated for 4 to 5 hours at 550° to 570°F. and subsequently thinned with turpentine or kerosene, it can be used for the preparation of very satisfactory lacquers and varnishes. The latter are stable to acids but not to alkalies.

Wagner and Schmidt (1933) review the methods of processing fish oils for paint and varnish purposes. The detrimental effects of the solid glycerides in these oils is reflected in the patent literature by the large number of proposals for their removal. German patents 272,465 and 273,347 mention distillation with superheated steam with or without the addition of catalysts, the free glycerine and fatty acids being carried off with the steam and leaving behind a residue with intense drying properties suitable for the manufacture of varnishes resistant to acid, alkali, water and tar. German patent 438,104 suggests the polymerization of fish oils after admixture of a vegetable drying oil by heating in a vacuum at a temperature just below the decomposition point of the oils. Wagner and Schmidt suggest that a promising way for the utilization of fish oils in paints is in the production of substances capable of inducing certain colloidal-chemical effects on addition to varnishes and paints. As examples of this they may be used as protective colloids for the prevention of pigment settlement, as wetting-out agents for reducing oil absorption, and as swelling agents for increasing the viscosity.

Aluminium salts of certain unsaturated fatty acids of fish oils considerably improve the elasticity and brushing qualities of both paints and varnishes. Satisfactory products are said to be produced by an oxidizing treatment of nitrocellulose-urea-formaldehyde resin in the presence of a fish oil at 338° to 356°F. (British patent 301,133). Finally, it is suggested by these authors that flour paste and alkaline starch solutions can be worked up with fish oils and pigments to produce the so-called Swedish paints which give excellent outdoor results on sea coasts.

L. J. Reizenstein (1936) states that in properly manufactured fish oils the bulk of the "waxy" constituents is removed, leaving for film-making purposes an extremely effective hard-drying polymer which is held in solid solution in the portion of the film of lower iodine value. This results in elasticity being retained. This author indicates the use of fish oils in the preparation of short, medium and long varnishes, all-oil types of varnishes, synthetic resin varnishes, paints, enamels and lacquers. Toch (1936) states that fish oils improve the life of aluminium-tung-oil spar varnishes. In a very interesting paper Buser (1938) reviews the use of fish oils in paint technology. He states that fish oils can be processed satisfactorily by heat polymerization, blowing with air, sulphurizing and by steam distillation. Buser also mentions the use of highly unsaturated fatty acids from fish oils for condensation with alkylphenols, and the condensation of fish oils with polybasic acids such as succinic, maleic and phthalic acids. Some work on the drying properties of fish oils was carried out by Ohl (1936). This author states that, even when stearine has been removed by chilling and the oil has been deodorized by blowing with steam, a fish oil may not be suitable for paint manufacture. Heat thickening is beneficial but blowing appears to be more advantageous, as it causes quicker drying and has other advantages when compounded into paints. Analysis of a series of blown oils shows that during blowing the unsaponifiable matter increases as does the acid value. The per cent of hydroxy fatty acids at first increases, then as blowing proceeds, decreases again. The iodine value, of course, decreases as blowing proceeds. Samples of the variously blown oils when plated out showed that the chemical changes taking place during the drying process were progressively smaller as the blowing time of the oils increased. During drying it was observed that there was a tendency for the oils to precipitate a resinous material and this tendency increased with increase in free-fatty-acid content of the oils.

In an article dealing with the practical utilization of fish oils in the paint trade, Alexander (1935) lists the uses of the various grades now commercially available. He states that stack paints are made from a refrigerated and pressed oil. In combination with linseed or tung oil it is used in barn paints and in industrial maintenance paints which are exposed to sulphur fumes. Kettled alkali-refined oils hold their colour well, deodorize easily with heat and are used in combination with other oils for mixed paints. They are said to give good washing and brushing properties to flat wall paints and in combination with tung oil make a good exterior cement paint. This combination with tung oil is also a good

vehicle for aluminium paints. Blown oils are used as a base for cold-cut paint oils and are usually clear and free from haze. They are used to make coloured asbestos roof coatings and are added to red, green and brown linseed-oil paints to prevent chalking, blistering and peeling. Thoroughly deodorized fish oils are now being used successfully in white enamels, flat wall paints and in interior and exterior mixed paints and undercoatings.

On the other hand Pfanner (1936) and Ohl (1938) find that paints and varnishes containing fish oils are inferior to those made with linseed or tung oils. The former investigator studied the use of fish, castor, and tung oils when used to replace linseed oil as a plasticizer for colophony or similar film-forming resins. The chief disadvantages of these materials were (1) the high content of volatile thinners required which resulted in the production of thin films, and (2) a tendency to react with certain pigments containing lead or zinc, thereby giving unusually brittle films. Ohl states that lacquers made with fish oil are slow drying and paints made with it have, in general, somewhat inferior properties to those containing only linseed oil, except when exposed to dilute acids where fish-oil paints sometimes show a higher resistance.

Some mention must be made of a new series of drying oils (Haco-oils), made for use in paints and varnishes, that has appeared in Germany. These are made from fish oils by an undescribed process and appear to show some outstanding properties, particularly when used in varnish manufacture. Burstenbinder (1936) has described these oils in some detail but gives no clue to the mode of preparation. He suggests that the outstanding drying properties are due to the presence of conjugated double linkages and likens the behaviour of these oils to that of tung oil. It is strange, however, that in the various published papers listing the chemical and physical characteristics of this series of oils no "diene" values are given. Scheifele (1937) claims that in the Haco series of oils the enhanced drying and film-forming properties are produced by treating fish oils so that (1) the content of solid glycerides is reduced, (2) natural antioxidants are removed, and (3) the excessive degree of unsaturation of the more highly unsaturated fatty acids is lowered by polymerization, oxidation and condensation. Again the process is not described, but one gathers that it includes a wintering and alkali-refining process followed by a modification of one of the steam-distillation methods for removal of some of the saturated fatty acids. Scheifele tabulates the results of tests with varnishes made with limed rosin, Albertol resin and ester gum with various grades of the Haco oils either alone or in combination with linseed or tung oil. The Haco-oils he used were described as follows:

Oil No. 1.
  Sp. G. at 15°C., 0.933; Engler visc. at 50°, 2.8; free fatty acids 4.5%; iodine value 165-175; sap. value 185-195; ox. fatty acids 0.5 to 0.8%; colour similar to "R.A." linseed oil.
Oil No. 2.
  Thickened by blowing with air. Sp. G. at 15°C., 0.933-0.988; Engler visc. at 50°, 100-200; free fatty acids 4-6%; colour like raw linseed oil, somewhat cloudy; very slight fish-oil odour.
Oil No. 3.
  Sp. G. at 15°C., 0.940-0.950; Engler visc. 8-9 at 50°; sap. value 187-195; colour like raw linseed oil; somewhat fishy odour.
Oil No. 4.
  Viscosity as in no. 3; darker colour, clear and no odour.
Oil No. 5.
  Viscosity and colour like "R.A." linseed oil. Clear.
  Data selected from those of Scheifele are given in table XLVIII. Only three out of five series given in the original report are shown here. The details of the production ot the varnishes in each series are given below.

TABLE XLVIII. Some properties of varnishes containing fish oil (Scheifele 1937).

Sample	Colour compared to iodine soln.	Drying properties of films					Physical and chemical properties of dried films aged 4 days							After baking Hardness to scratching		
							Resistance to abrasion	Hardness to scratching	Flexibility	Water marks	Under water 16 hours in the cold	5% soda	10% salt			
Series 2		2.5 hrs.	4.5 hrs.	7.5 hrs.	24 hrs.	48 hrs.	Series 2 Lime-resin varnishes							2.5hrs.	4.5hrs.	6hrs.
Linseed-Tung oil	n/10	tacky	tacky	partly tacky	not dust dry	dry	150	8-9	cracked	distinct	intact	scarcely attached after 0.5 hours	intact	7	7-8	8
Fish oil no.1-Tung oil	n/40	tacky	tacky	still tacky	not dust dry	dry	200	7	cracked	none	dull	broken down	intact	7	7-8	8
Fish oil no.5-Tung oil	n/10	tacky	tacky	still tacky	slightly dry	dry	200	8	cracked	none	white	broken down	intact	7-8	7-8	8
Fish oil nos. 3 & 2-Tung oil	n/10	tacky	tacky	distinctly dry	dry	dry	200	8	cracked	none	white	broken down	intact	6-7	7-8	8
Series 4		2 hrs.	4.5 hrs.	7 hrs.	23 hrs.	72 hrs.	Series 4 Albertol varnishes							3-5hrs.	4-5hrs.	7 hrs.
Linseed-Tung oil	n/100	drying	partly tacky	partly tacky	almost firm	dry	100	8	cracked but adhered	none	clear	after 10 hours no effect	intact	4	8	8
Fish oil no 2-Tung oil	n/10	partly dry	very tacky	more tacky	less firm	dry	100	7-8	cracked but adhered	none	clear	after 10 hours no effect	intact	5	8	8
Fish oil no.5-Linseed-Tung oil	n/40	partly dry	very tacky	more tacky	fair	dry	100	9	cracked but adhered	trace	clear	after 10 hours no effect	intact	3	7	7
Series 5		3 hrs.	5 hrs.	22 hrs.	48 hrs.	72 hrs.	Series 5 Resin-ester varnishes							3 hrs.	5 hrs.	7 hrs.
Linseed-Tung oil	n/20	very tacky	still tacky	dry	almost firm	dry	100	8	cracked but adhered	trace	intact	after 10 hours no effect	intact	4	7-8	7-8
Fish oil no.1-Tung oil	n/20	very tacky	still tacky	slightly tacky	almost dry	dry	100-150	8	cracked	trace	intact	after 10 hours no effect	intact	7	8	7-8
Fish oil no.6-Tung oil	n/40	very tacky	still tacky	slightly tacky	almost dry	dry	100-150	7	cracked	trace	intact	after 10 hours no effect	intact	3	8	8
Fish oil no.5-Tung oil	n/10	moderate	tacky	slightly tacky	almost dry	dry	100	8	cracked	trace	intact	after 10 hours no effect	intact	6	7-8	8

SERIES 2. Limed rosin varnishes. Ratio of oil to rosin, 1:1.

Varnish 2:1 Linseed-tung oil. 25 parts tung oil heated with 50 parts rosin at 290°C. and 25 parts linseed oil added. Heated for ½ hour at 275°, ¼ hour at 290°. and ¼ hour at 305°C. After cooling to 150°C, 2 parts of drier and 75 parts thinner added.

Varnish 2:4 Fish oil no. 1-tung oil. As in varnish 2:1 with fish oil no. 1 replacing the linseed oil. After addition of fish oil heated to 310°C. for 35 minutes and to 320°C. for a short time. Driers and thinners as above.

Varnish 2:5 As in 2:4 but fish oil no. 5 used to replace linseed oil.

Varnish 2:6 20 parts tung oil and 20 parts fish oil no. 3 with 60 parts rosin heated to 290° C., then 20 parts of fish oil no. 2 (blown oil) added slowly. Driers and thinners added as above.

SERIES 4. Albertol resin varnishes. Ratio of oil to resin, 1.5:1.

Varnish 4:1 Linseed-tung oil. 50 parts tung oil heated to 160 to 180°C. and 50 parts Albertol resin added. After resin had dissolved, mixture heated to 310°C. for 15 to 20 minutes. 25 parts thickened linseed oil then added and heating continued for a short time at 320°C. When cooled sufficiently, 3 parts soligen-cobalt-lead-manganese drier added and 50 parts of thinner.

Varnish 4:2 Fish oil-tung oil. 50 parts tung oil, 50 parts of Albertol resin and 25 parts fish oil no. 2 processed as in 4:1.

Varnish 4:3 Fish oil-tung oil. 25 parts tung oil and 25 parts fish oil no. 5, 50 parts Albertol resin and 25 parts fish oil no. 2, processed as in 4:1.

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Varnish 5:1 Linseed-tung oil. 25 parts tung oil heated to 160° to 180°C. and 50 parts of gum added. Temperature raised to 275°C. and 25 parts of lacquer grade linseed oil added. Mixture held at 280° to 290°C. for 50 minutes and then cooled to 180°C., after which 1/8% solid soligen-cobalt drier added and thinned with 50 parts solvent.

Varnish 5:4 Fish oil-tung oil. Same as 5:1 but fish oil no. 1 replacing linseed oil. After addition of fish oil mixture heated for ½ hour at 310°C. Remainder of process same as in 5:1.

Varnish 5:5 Fish oil-tung oil. As in 5:1 but fish oil no. 6 replacing linseed oil. After addition of fish oil heated at 310°C. for ½ hour.

Varnish 5:6 Fish oil-tung oil. As in 5:1 but fish oil no. 5 replacing linseed oil. After addition fish oil, heated ½ hour at 310°C.

The resistance to abrasion of the varnish films was measured by the weight in grams of no. 220 silicon carbide falling through 35 cm. required to produce a distinctly visible abrasion mark on the varnish film dried on glass. The hardness to scratching was found by the Wolff-Wilborn method using a 300 gram weight and Faber-Castell lead pencils ranging from 6B to 7H. Other methods of testing are obvious from the data in the table.

The data indicate that varnishes containing fish oil took a little longer to dry thoroughly than those containing an equal amount of linseed oil. However, the mechanical properties of the films were good. The hardness to scratching was practically the same as for linseed-oil varnishes whilst the resistance to abrasion and flexibility were higher throughout. In waterproofness and stability towards chemical reagents the fish-oil varnishes were practically equal to the linseed-oil varnishes; at most, the water resistance was but slightly inferior. Both types of varnishes behaved similarly on baking. Scheifele therefore concludes that the use of these particular fish oils is entirely justified in the manufacture of varnishes.

(iv) OPINIONS OF PRACTICAL MANUFACTURERS

In a recent survey carried out by the writer a questionnaire was sent to all major paint companies in Canada asking their frank opinion as to whether Canadian pilchard oil could be considered to be of any value in the paint and varnish industry. Fourteen out of 15 firms replied in the affirmative and in addition offered some very interesting and instructive observations, a summary of which is included here.

Nearly all firms use a medium or heavy pressed oil and some require an oil with a cloud test of 2 hours at 32°F. These oils exhibit slow drying properties and the film possesses an after-tack which is very noticeable during warm humid weather. Drying properties can be improved by blowing or heat-bodying. Odour is also eliminated by these processes. The bodied oils give films that dry satisfactorily in cool weather but, when the temperature rises above 75°F., a tackiness is produced that may last for 7 to 10 days. This tackiness may be overcome by the use of cobalt or manganese driers, but these impart a colour to the oil that makes them of little value for white or light-coloured paints. Tackiness can also be overcome by combining with tung, perilla or linseed oils or by the use of various kinds of synthetic resins. Blown pilchard oil, although drying better than the

raw oil, has a tendency to yellow in the package; this tendency is not possessed by the heat-bodied oil. All manufacturers agree that the blown and heat-bodied oils are satisfactory as far as odour is concerned.

Among the products in which pilchard oil is now successfully being used the following were mentioned: smoke-stack blacks, barn and structural steel paints, shingle stains, and external paints where durability is not a primary factor. Many firms state that the use of pilchard oil is gradually increasing as proper formulations are learned that take into account the softer nature of the film. It cannot be classed as a substitute for linseed, perilla or oiticica oils but rather as an adjunct to these oils. However, some manufacturers think that it can replace soya-bean oil where after-yellowing is not an important factor and that mixtures of pilchard and tung oil can successfully replace perilla oil in some formulations.

(v) INFLUENCE OF VARIOUS MATERIALS ON OXYGEN ABSORPTION OF PILCHARD OIL

Since it is recognized that of all the Canadian marine animal oils now produced in commercial quantities, pilchard oil is the only one that has properties of interest to paint and varnish manufacturers, it is of interest to consider in some detail the oxidation, drying properties and film properties of this oil. In Section 5 I (c) and Section 6 some reference has already been made to the rate of oxidation of pilchard oil under certain conditions, particularly the effects of various refining processes and the behaviour of the oil when blown with air at high temperatures. The main subject of the present section will therefore be the action of various driers and pigments on the oxygen absorption of the oil and a consideration of the effects of a few miscellaneous processing treatments. The data are taken principally from the work of Denstedt and Brocklesby (1936a).

In order to compare the influence of various metals on the rate of oxidation of pilchard oil, driers were prepared by making soaps of pilchard-oil fatty acids and various metals and then dissolving the soaps in pilchard oil. The metallic soaps were made by adding solutions of inorganic salts of the different metals to aqueous solutions of the potassium soaps of pilchard-oil fatty acids. The soaps precipitated out, some as hard, horny masses, others in a more spongy form. These soaps were then dissolved in pilchard oil (about 65 grams of the moist soap in 270 grams of oil) by heating in an inert atmosphere for two hours at 160°C. (320°F.). The metal contents of the resulting solutions are given in table XLIX. These solutions were not necessarily saturated as the solution of the various soaps in the oils was retarded by the moisture in the soaps. The oil-soap solutions were diluted with pilchard oil so as to make the concentration 0.03 per cent, calculated as the monoxide of the metal. This concentration was chosen because it was the limit of solubility in the case of some of the metals. The soaps of cerium, nickel and the alkaline-earth metals gave the most frothing during the preparation of the concentrated drier solutions, cobalt and manganese slightly less and the remainder gave little, if any, frothing. Copper and iron soaps dissolved to a slight extent in the cold to give brilliant green and brick-red solutions, but on heating, the solutions turned dark.

The lead compounds were by far the most soluble of the driers examined. The hot solutions were usually clear but dark, and on cooling deposited considerable precipitate. If this precipitate was removed and the clear solution allowed to stand for a few days a further precipitate developed until a kind of equilibrium was established. By removing the solids when equilibrium was reached, several successive precipitations could be obtained. The precipitate, which when purified was a crystalline white powder, contained 40 per cent lead and the fatty acids isolated

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TABLE XLIX. Metal content of pilchard oil soap driers

Metal	Metal content as oxide (%)	Metal	Metal content as oxide (%)
Cobalt..............	0.08	Manganese..........	....
Lead................	8.80	Cerium..............	0.13
Uranium............	0.14	Copper..............	0.05
Iron................	0.03	Nickel..............	0.27
Zinc................	0.28	Chromium...........	....
Cadmium...........	....	Aluminium..........	0.17
Magnesium..........	0.03	Barium.............	0.04
Calcium............	0.11	Strontium...........	0.03
Mercury............	0.06		

from it had a m.p. of 50.5°C., iodine value 1.2 and mean molecular weight of 254. It is probable, therefore, that this precipitate was the lead salt of the solid fatty acids of the pilchard oil originally saponified. Such a precipitate may also be caused by the action of lead driers on pilchard oil itself because similar solids are deposited when lead oxide is heated with neutral pilchard oil or when the lead salts of linseed-oil fatty acids are dissolved in neutral pilchard oil in the cold.
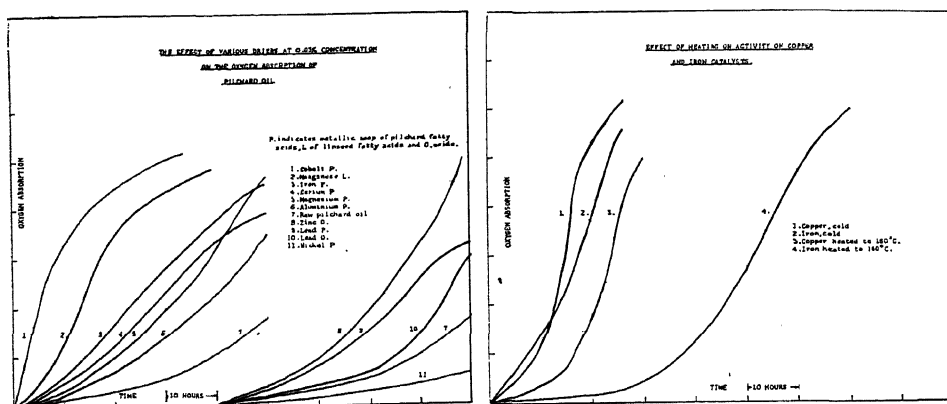
FIGURE 64. Effect of some driers on oxygen absorption of pilchard oil.

Many other metals have the same tendency to precipitate but to a much smaller extent. Lead tungate (lead soap of tung-oil fatty acids), in as low a concentration as 1 per cent, will in time give precipitates of solid lead soaps. Cobalt has only a slight tendency to precipitate solid soaps from a concentrated solution in pilchard oil; the precipitation is greater in the case of the manganese soaps. Vanadium, bismuth, antimony and tin compounds were found to be converted into the oxides when heated in pilchard oil. The oxides were dispersed in the colloidal form and remained in suspension even after standing for over a year. All these solutions were opaque and quite dark.

The effect of some of these driers on the oxidation of pilchard oil are shown graphically in figure 64. Relatively few show any outstanding effects. The most active were cobalt and manganese, followed by copper, iron, cerium, aluminium and lead. The activity of the other driers may not always follow the order given in the figure but their average activity is fairly well indicated. Since cobalt and manganese showed so much superiority in catalytic activity,

tests were made to find optimal concentrations and temperatures of incorporation. The results showed that the maximal effects were given by approximately 0.05 cobalt oxide and from 0.15 to 0.20 per cent of manganese oxide incorporated in the oil at a temperature of 125°C. (257°F.).

Some pigments used in paint manufacture have an effect on the rate of oxidation of the oil vehicle. In some cases this is due to adsorption of the drier by the pigment while in others the pigment itself may exert an accelerating action. This tendency was investigated by thoroughly grinding 10 grams of the pigment in 100 grams of pilchard oil, heating the mixture for 15 minutes at 160°C. (320°F.), cooling and determining the oxygen absorption in the usual manner. The data are given in figure 65 and show that umber and white lead, containing manganese and lead respectively, have an accelerating action, a fact well known in paint technology. The green and yellow chromes had but little effect, but zinc oxide and inert materials such as graphite, silica, Filtrol and carbon black had definite retarding effects. In general, these results are similar to those obtained with linseed oil. The adsorptive effect of inert materials was further shown by treating pilchard oil containing cobalt and manganese driers with Filtrol. If the linoleates of these metals are dissolved in the oil, little if any of the metallic soap is removed by the Filtrol, but, if small amounts of the oxides are incorporated in the oil by heating, they become colloidally dispersed to clear solutions, from which the oxides can be removed by treatment with Filtrol. These data are shown in figure 65.
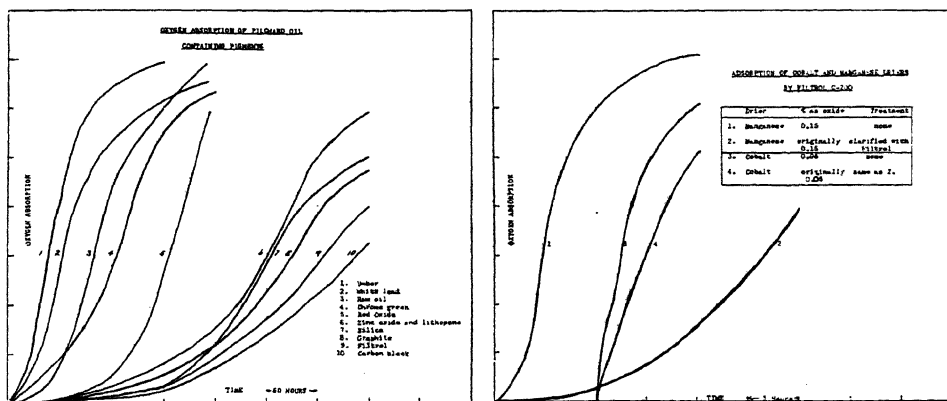
FIGURE 65.   Effect of some pigments on oxygen absorption of pilchard oil.

Pilchard oil polymerized by heat in an inert atmosphere showed an increased inductive period of oxygen absorption, which was proportional to the time and temperature of heating. The rate of oxidation at the end of the inductive period was also retarded, and the total amount of oxygen absorbed was reduced. Oils thickened by ultraviolet-light irradiation showed a decrease in inductive period, but the total amount of oxygen absorbed was slightly diminished. Blown pilchard oil, as with other oils, shows no inductive period and oxidizes rapidly, but absorbs less oxygen than the unblown oil. The treatment of pilchard oil with dry sulphur dioxide gas entirely eliminates the inductive period of the oil, but has little effect on the subsequent rate of oxidation. It appears that the gas destroys the antioxidants present in the raw oil, but, from a consideration of the film properties of the treated oils, it is also evident that the unsaturated fatty acids themselves are in some way affected.

(vi) FILM PROPERTIES OF PILCHARD OIL

Denstedt and Brocklesby (1936b) show by physical and microscopical methods that the characteristic defects of pilchard and other drying fish-oils are inherent

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qualities, dependent upon the composition of these oils. The composition of fish body oils has already been dealt with in Section 2 of this Bulletin and the differences in composition between such oils as pilchard and linseed are at once very apparent. Pilchard oil contains about 23 per cent of saturated fatty acids; linseed oil contains about 7 per cent. Of the unsaturated fatty acids, pilchard oil contains approximately 11 per cent with 1 double bond, 35 per cent with from 1.5 to 2.4 double bonds, 14 per cent with 4 double bonds and 15 per cent with 5 double bonds. On the other hand linseed oil contains about 5 per cent with 1 double bond, 48 per cent with 2 double bonds and 35 per cent with 3 double bonds. The unsaturated fatty acids in linseed oil all belong to the C_{18} group of acids, whilst those in pilchard oil extend from the C_{16} group to the C_{24} group. It is not surprising, therefore, that these two oils should show great differences in the properties of their dried films. If pilchard oil is to be used as a legitimate drying oil it is essential that these differences should be thoroughly appreciated and understood by the trade. A detailed summary of this paper by Denstedt and Brocklesby is therefore included here.

A. *Microscopical structure of pilchard oil films*

When a film of oil "dries", the transition from the liquid to the solid state involves many complex chemical and physical changes that are, even yet, not completely understood. Chemically, the reactions involved include oxidation, condensation, polymerization and possibly isomerization. Physically, the drying process can be divided into at least 4 main stages, namely: (1) a period of induction, (2) formation of micelles, (3) coagulation of micelles to form a gel, and (4) subsequent changes in the gel. As these changes progress, the oil decreases in unsaturation and increases is viscosity. When coagulation begins, the film takes on a definite structure, the nature of which depends upon the sequence of chemical changes and hence on drying conditions. Although the gel possesses definite structure it is still fluid and sticky and it is not until the fourth stage that actual drying or solidification occurs. The final structure of the film is modified further by the presence of components which are non-drying and therefore do not contribute to the film formation. The first three stages of the film-forming process may be accomplished without oxygen, as for instance in steam-polymerization, but for the final formation of a dry tough film, oxygen is necessary.

As drying takes place more rapidly at the exposed surface, solidification begins there and proceeds inwards. The film therefore consists of two more or less distinct layers, namely, the solid surface layer and the inner less compact portion. This heterogeneous structure is shown by the photomicrographs in figure 66, where it is apparent that the film still consists of two layers, the outer being homogeneous and the inner, although transparent, being quite conglomerate in its make-up. This type of structure is more marked in fish oil than in linseed oil films and is due to the accumulation of the solid non-drying components in the under layer. It is probable that, as the surface layer solidifies and becomes more compact, the non-drying and semi-drying components become insoluble in that layer and are forced into the interior of the film. This process is evidenced by double drying. If a film which has been dried on mercury for several days is reversed until the underside has thoroughly dried, a cross-section will reveal the solid constituents sandwiched between the two clear surface layers. In a freshly prepared film the solids are distributed in finely divided form uniformly throughout the film except in the clear layer at the surface. On aging of the film, the small solid particles in the inner portion gradually collect to form larger spherical crystalline masses. In oven-dried films the crystalline region is confined to the innermost portion of the film, indicating that the solids are squeezed out of the highly oxidized surface layer of the film. The spherical crystalline masses vary in diameter and are commonly seen in aged sections of oven-dried pilchard-oil films but have not as yet been

detected in linseed-oil films. By extraction and purification with alcohol it has been ascertained that the crystalline masses consist of a mixture of saturated glycerides and fatty acids. The crystals soften at about 49°C. and melt between 55° and 57°C. The mixture also contains a component with a melting point of about 80°C.
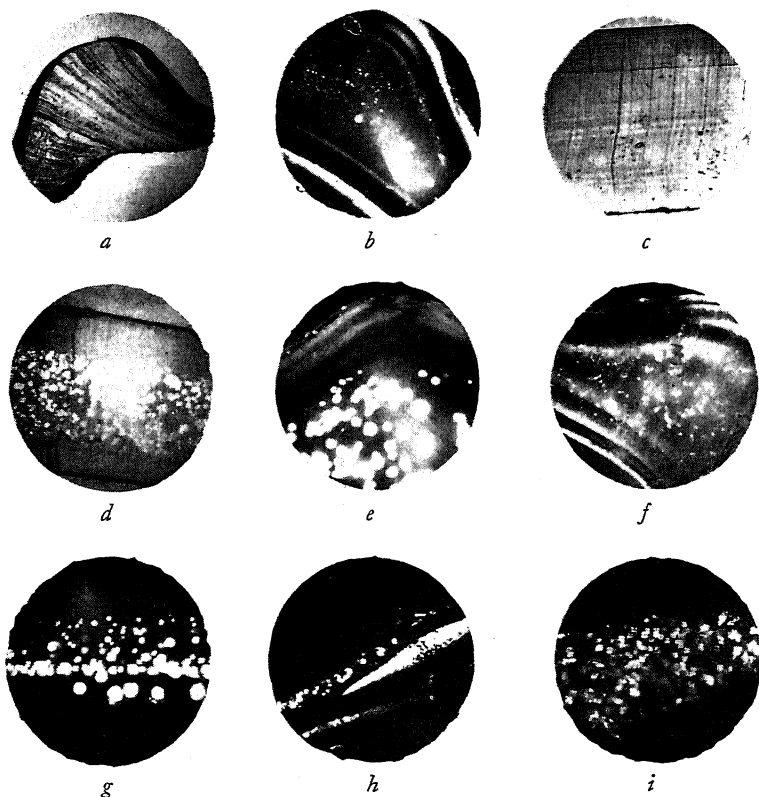
FIGURE 66. *a*,—Section of wrinkle of linseed oil film viewed through uncrossed nicols. Dark outer areas are surfaces of the film to be disregarded. *b*,—Section of linseed oil film wrinkle viewed through crossed nicols. Note the clear surface layers and the less dense inner portion containing crystalline solids. *c*,—Section of pilchard oil film under uncrossed nicols. Film diam. 1.4 mm. *d*,—Section of pilchard oil film under half-crossed nicols. Note the inner portion of film which is less dense and contains crystalline bodies. *e*,—Section of pilchard oil film showing transparent clear outer layer and softer inner portion containing solid crystalline masses. Viewed under half-crossed nicols. *f*,—Section of a linseed oil film showing the relative absence of crystalline solid components in the inner portion. Half-crossed nicols. *g*,—Crystalline portion of pilchard oil film as viewed through fully crossed nicols. *h*,—Section of a wrinkle of a menhaden oil film—under crossed nicols. *i*,—Inner portion of a pilchard oil film showing sphero-crystalline character of many of the solid masses. Crossed nicols.

B. *Influence of driers.*

The influence of certain metals, introduced as the metallic soaps of pilchard-oil fatty acids, on the drying time and gain in weight of pilchard oil is shown in table L. Parallel with their

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effect on oxygen absorption, cobalt and manganese surpass all other metals in their drying activity. Cobalt is superior in some ways to manganese. It is more active as a drier, imparts less colour and produces harder, less tacky films. On account of their activity both these metals sometimes produce surface or "skin" drying. Lead, cerium, iron and copper form a class by themselves

TABLE L. Influence of various metals on the drying time and gain in weight of pilchard oil

Metal	Drying time (hours)	Gain in weight (%)	Metal	Drying time (hours)	Concentration as oxide (%)
Co..........	20	9.0	Co..........	10	0.08
Mn.........	24	9.5	Mn.........	13	0.1
Cu.........	150	8.8	Pb.........	30	8.8
Bi..........	156	9.5	Ce.........	48	0.13
Fe..........	156	10.0	Fe.........	48	0.6
Cd.........	163	8.4	Al.........	48	0.17
Pb.........	186	11.0	Ca.........	48	0.11
Ce.........	186	10.0	Sn.........	48	0.53
Ca.........	186	11.0	Cu.........	60	0.04
Mg.........	188	10.0	U.........	60	0.14
U.........	206	11.0	Cd.........	60	....
Sb.........	210	10.5	Mg.........	60	0.06
Zn.........	210	11.0	Sb.........	60	....
Al.........	216	10.5	Ni.........	72	0.27
Ni.........	218	10.5	Cr.........	72	....
Cr.........	218	10.5	Bi.........	96	....
Sn.........	226	10.5	Zn.........	96	0.28
Ba.........	222	....	Ba.........	96	0.04
Hg.........	223	20.0	Sr.........	96	0.03
Sr.........	223	10.5	Hg.........	120	....
			V.........	120	....
Raw oil.....	400	11.0	Raw oil.....	267	....

because of certain effects they have on gelation and solidification. Although these metals eliminate the inductive period, they have little effect on the rate of subsequent oxygen absorption. They produce a rather rapid increase in viscosity to the stage where the film is almost semi-solid. After remaining in this state for some time the film solidifies rather abruptly. This is particularly noticeable with cerium driers. Copper and iron tend to promote disintegration of the dried film and therefore cerium and lead can be said to be the only satisfactory driers that can be used to promote uniform drying and to counteract skin drying. Antimony, nickel and tin showed a slight tendency to harden the film but not immediately after drying.

C. *Hardness of pilchard-oil films.*

Films made from raw and cold-cleared pilchard oil are inferior in hardness and tensile strength to those made from linseed oil. On the other hand the former possess greater flexibility and stretching capacity than do the latter. Unfortunately, any treatment that improves hardness usually detracts from flexibility. Another defect of fish-oil films is their tackiness which persists even when driers are used. Films made from fish oil alone therefore collect dust rapidly and become dull. Softness and tackiness have a common origin in the incompleteness of film structure which is due to the presence of excessive amounts of non-drying components. The components that interfere with the proper drying of fish oil films are the glycerides that con-

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tain a preponderance of non-drying saturated and mono-ethylenic fatty acids. In addition there are also present some glycerides that contain both drying and non-drying fatty acids. Only those glycerides that contain a preponderance of drying fatty acids can contribute to the formation of a satisfactory film. The presence of non-drying fatty acids is therefore a detriment. The nature of the non-drying fatty acids determines the type of failure in the film. Liquid or semi-solid monoethylenic fatty acids absorb oxygen but do not dry; they are responsible for tackiness. Solid saturated fatty acids do not absorb oxygen but make a film dull and soft.

TABLE LI. Relative hardness (grams weight necessary for puncture) of pilchard-oil films containing various driers

Drier	G.	Drier	G.
Cobalt soaps....	42	Strontium soaps..	42
Manganese soaps	42	Magnesium soaps	37
Lead soaps.....	42	Mercury soaps...	32
Lead oxide.....	62	Antimony.......	62
Cerium soaps...	62	Bismuth.........	42
Copper soaps...	42	Vanadium.......	27
Iron soaps......	62	Tin.............	72
Aluminium soaps	37	Lithium.........	42
Nickel soaps....	67	Cobalt acetate...	52
Chromium soaps.	42	Cobalt resinate...	67
Uranium soaps..	42	Cerium resinate..	72
Cadmium soaps.	37	Cobalt-cerium....	92
Zinc soaps......	42	Cobalt-lead......	22
Calcium soaps...	42	Ferrous sulphate.	82
Barium soaps...	42	Cobalt linoleate..	72

For the proper preparation of fish oils for use in paints and varnishes, therefore, these non-drying components have to be reduced in amount or eliminated entirely. Cold-clearing (wintering) tends to reduce them, but even the most highly wintered fish oil still contains sufficient non-drying fatty acids to make a soft tacky film. Polymerization followed by steam distillation, however, produces a film that is entirely free from these detrimental components and the films are hard and free from tack. Increased temperature and humidity diminish hardness and increase tackiness. This is due to some extent to the softening of some of the solid constituents, but it is also associated with a reversible dissociation of the film structure. This dissociation is hastened by moisture, but films that have become quite tacky on exposure to a high humidity become quite hard in a few hours if kept in a dry atmosphere. Light also has an effect on hardness and tackiness. Films dried in the light are usually harder and less tacky than those dried in the dark. This effect varies with the wave length of the light. It is greatest with ultraviolet and diminishes towards the red.

The relative effects of various driers on the hardness of pilchard oil films are shown in table LI. Cerium, especially in conjunction with cobalt, gave the best general results. It is interesting to note that cobalt linoleate gave much harder films than the cobalt soaps of pilchard-oil fatty acids. The hardening effect of ferrous sulphate is, of course, well known to paint technologists. That films do not immediately attain their maximal hardness after the initial drying period is well brought out in table LII. Cobalt-containing films attained maximal hardness in 35 hours, whilst those containing lead required almost 200 hours. Air-blown pilchard oil dried harder and more quickly than heat-polymerized oil. Heat-polymerized pilchard oil with gum dried slowly, but reached a higher degree of hardness than the oil alone. Steam-bodied pilchard oil gave the best results of all; it dried rapidly and attained great hardness.

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TABLE LII. Increase in hardness (grams weight necessary for puncture) of various samples on drying at 25°C.

Hours.					10	20	35	70	190
Refrigerated pilchard oil									
+cobalt	Dry	22	37	52	72	82	122	117	121
+lead	..	..	..	..	..	..	..	67	102
bodied+cobalt	..	Dry	12	22	22	42	47	67	62
air-blown+cobalt	Dry	27	48	62	77	97	117	112	112
bodied + amberol gum + cobalt	..	Dry	32	72	72	97	127	137	172
steam-bodied + cobalt dissolved in turpentine	Dry	72	230	430	..	over 2000	..	over 7000	..
steam-bodied (slightly less)+cobalt in carbon tetrachloride				Dry	20	32	72	162	382
Linseed oil+cobalt					42	92	197	232	192
China wood oil +cobalt	Dry-films discarded because of wrinkling. Hardness over 2000.								

Treatment of pilchard oil with sulphur dioxide gas was found to accelerate drying, most films becoming dust-dry in about two hours less than the untreated samples. The hardness of the resulting films was about 100 per cent greater than those of the untreated. However, films of sulphur-dioxide-treated pilchard oil were stiffer and more easily cracked on bending; exposure tests showed that they were only about two-thirds as durable as the untreated.

As mentioned before, heat polymerization followed by steam distillation is the most effective way of overcoming the natural defects of pilchard oil films. The details of the process have been given in Section 8. The product of this treatment (when thinned with a suitable solvent) dries very rapidly with the aid of a small quantity of soluble cobalt drier. The resulting films are free from all the defects of ordinary films. They are glossy and absolutely free from tackiness. Furthermore, they possess very low permeabilities to moisture and are practically free from the tendency to turn yellow in the dark. In appearance, they are like varnish films in gloss and evenness of surface. In figure 67a is shown a photomicrograph of a section of steam-distilled oil film about 1 mm. in thickness. The surface layer is extremely hard and shows conchoidal fracture when cut or broken. Some of the solid components still remain in the film but these never diffuse through the dense keratin-like surface layer. Hence these films do not bloom.

Oven drying and baking of films are methods of improving hardness and reducing tackiness with obvious limits of application. The use of fish oils in baked finishes warrants some consideration of these methods, however. The effect of oven treatment at 100°C. (212°F.) on hardness is shown in table LIII. In oven-drying the oil is oxidized more rapidly and volatile components are driven off. Polymerization therefore takes place more completely and consequently the film structure is more compact. At temperatures as low as 60°C. (140°F.) pilchard-oil films dry hard and free from tackiness whilst at higher temperatures the hardness is greatly increased and at the same time the weight is diminished from loss of volatile material. At 160°C. (320°F.) the apparent loss in weight of pilchard-oil films varies from 6.6 to 9.0 per cent, except in the case of oils containing zinc, where there is an apparent gain. Oils containing cobalt and manganese suffer slightly less loss than those containing other driers, presumably due to greater oxygen absorption. Pilchard-oil films with driers darken considerably on oven baking; those without

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TABLE LIII. Influence of heat treatment at 100°C. (212°F.) on hardness of films (grams weight necessary for puncture)

Oil	*Original hardness	After heating at 100°C. for		
		30 min.	60 min.	90 min.
Raw pilchard..................	66	87	over 3,000	....
Raw menhaden................	40	57	57	over 3,000
Raw linseed..................	500	530	1,700	over 3,000
Steam-distilled pilchard.........	...	1,900	over 3,000	....

*Films were kept three weeks at ordinary temperature before testing.
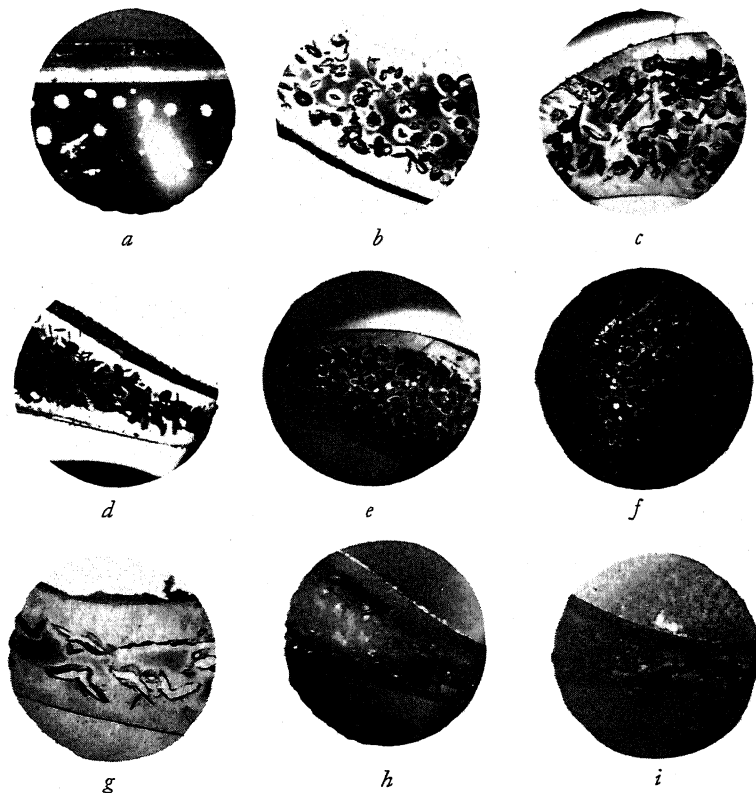
FIGURE 67. *a*,—Film from steam-bodied oil (thickness about 1 mm.) under crossed nicols. *b* and *c*,—Pilchard oil film partly dried after saturation with moisture. Note the cavities and opacity in the inner layer. Uncrossed nicols. *d*,—Pilchard oil film completely saturated with moisture. *e*,—Pilchard oil film containing moisture as viewed through partly crossed nicols. *f*,—Film viewed through fully crossed nicols showing crystal linings of cavities. *g*,—Section of a pilchard oil film which had been saturated with moisture and then placed in boiling water for one minute. *h*,—The formation of crystalline bloom on the surface of the film as viewed through crossed nicols. (Film had been exposed to excessive moisture). *i*,—Similar film viewed through partly crossed nicols.

drives do not change to such an extent. Another defect that appears after oven treatment of pilchard-oil films is "blooming" or the gradual accumulation of crystalline fatty acids and glycerides on the surface of the film to produce a dull whitish coating. Films dried at moderate temperatures show blooming the most; at higher temperatures more of the saturated fatty acids are driven off and consequently blooming is less pronounced.

D. *Effect of moisture.*

The capacity of drying-oil films to absorb and transmit moisture varies with the number and size of the film capillaries and therefore diminishes with increased density or compactness of the film. Ordinary fish-oil films are more permeable to moisture and gases than are those of linseed oil. Although the absorption of moisture by a film may bring about certain chemical effects, the physical effect of swelling is by far the most important. Swelling takes place to a
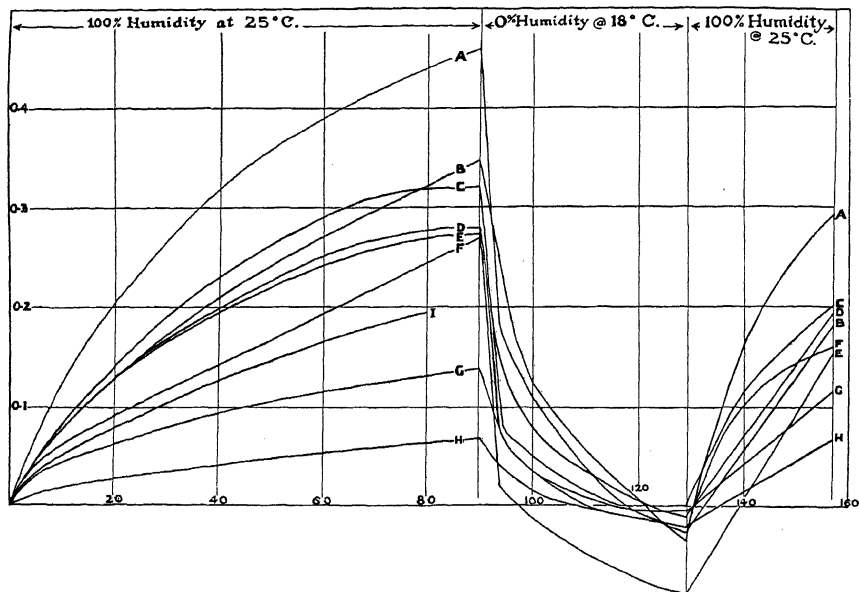
FIGURE 68. Moisture absorption of solid films. A,—Pilchard oil treated with sulphur dioxide. B,—Raw pilchard oil with cobalt drier. C,—Raw linseed oil with cobalt drier (wrinkled). D,—Pilchard oil blown with air at 160°C. E,—Wintered menhaden oil with cobalt drier. F,—Boiled pilchard oil+gum. G,—Bodied pilchard oil. H,—Steam-distilled bodied pilchard oil. I,—Linseed oil (non-wrinkled) very slightly bodied.

greater degree in the soft interior of the film and thus has two destructive effects: (1) it tends to detach the film from the surface to which it adhered, and (2) the differential swelling tends to destroy the integrity of the coating. So long as moisture can escape from one side of the film as rapidly as it is absorbed from the other, very little swelling occurs. Under extreme conditions of moisture, disintegration through swelling may be very rapid. For instance, a brown pilchard-oil paint, dried in a desiccator for several days, was placed in a cabinet saturated with moisture at 25°C. (77°F.). In 12 hours it had lost its adhesiveness and in expanding had slid along the plate in all directions from the centre so as to hang over the edges of the plate. The total expansion was about 5 per cent of the area. On placing in an oven at 60°C. (140°F.), contraction

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took place within 5 minutes. After baking for 6 hours the plate was again placed in the moisture cabinet. This time the expansion was practically negligible. Preliminary baking of a film diminishes greatly the tendency towards swelling.

On absorbing moisture, films gradually become non-transparent and dull, owing to the condensation of water on the walls of the capillaries in the less compact portions of the film. Transparency is usually lost at a moisture content between 5 and 5.5 per cent.

The relative rates of absorption of moisture by various films is shown in figure 68. The films were exposed in a cabinet saturated with moisture at 25°C. for a period of 90 hours, after which they were placed in a desiccator over calcium chloride at 18°C. (64°F.) for a period of 39 hours. They were then replaced in the moisture cabinet. The data showed that ordinary fish-oil films not only absorb moisture more rapidly than linseed-oil films but possess a high capacity for moisture. Sulphur dioxide treatment and air-blowing increase moisture absorption whilst the incorporation of gums, heat polymerization and steam distillation greatly decrease
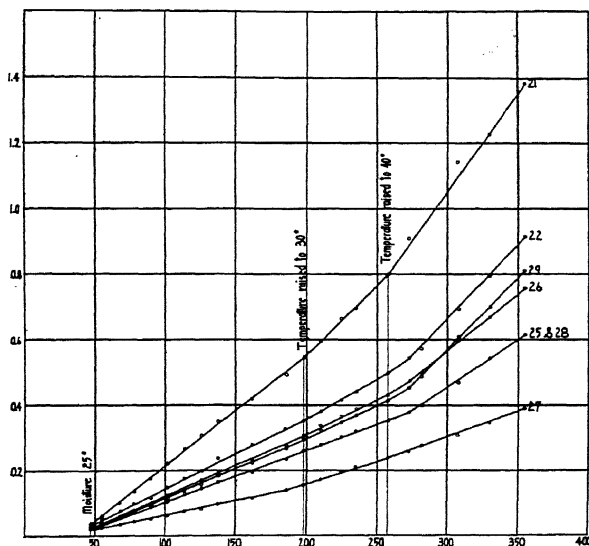
FIGURE 69. Permeability of films to moisture. 21,—Pilchard oil+cobalt. 22,—Linseed oil+cobalt. 25,—Pilchard oil containing rosin+cobalt. 26,—Menhaden oil+cobalt. 27,—Steam-bodied pilchard oil+cobalt. 28,—Steam-bodied pilchard oil+cobalt (less body). 29,—Air-blown pilchard+cobalt.

the absorption. The films of steam-distilled pilchard oil showed the least absorption of any oil examined. All films showed a more rapid absorption of moisture during the second exposure, i.e. after thorough drying.

In figure 69 data are given showing the water permeability of some films at three temperatures. The permeability is constant at any temperature, but the rate of transmission is not always strictly proportional to the temperature. For instance, the rate for air-blown pilchard oil was less than that of menhaden oil up to 30°C. (86°F.), but greater at 40°C. (104°F.). On the other hand the increase in rate at 40°C. in the case of the steam-polymerized oil film was not as great as might be expected from a comparison of the rates at 25° and 30°C. The permeabilities are affected by various treatments in the same way as are the absorptions.

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The tendency of oil films to become yellow during aging is an important consideration in paint and varnish manufacture. Tung-oil films are notorious in this respect, whilst poppy-seed and soya-bean oils are practically free from it. Linseed-and-fish-oil films lie between these extremes, the latter approaching tung-oil films in yellowing tendency. Whilst our knowledge of yellowing is still very indefinite, it is generally agreed that it involves intermediate oxidation products and that it is apparently accelerated by moisture, certain driers, pigments and the absence of short-wave visible light. In figure 70 some illustrations are given concerning the effect of light on the yellowing of pilchard-oil films. These are self-explanatory. As far as the correction of yellowing of fish-oil films is concerned, it has been found that for raw refrigerated pilchard oil cobalt driers give slightly less yellowing than manganese or lead. The use of a small amount of benzoyl peroxide also has a slight beneficial effect. Sulphur dioxide treatment completely eliminates after-yellowing; white paints made from sulphur-dioxide-treated pilchard oil have retained their whiteness and hardness after being kept in the dark for three years. Steam-
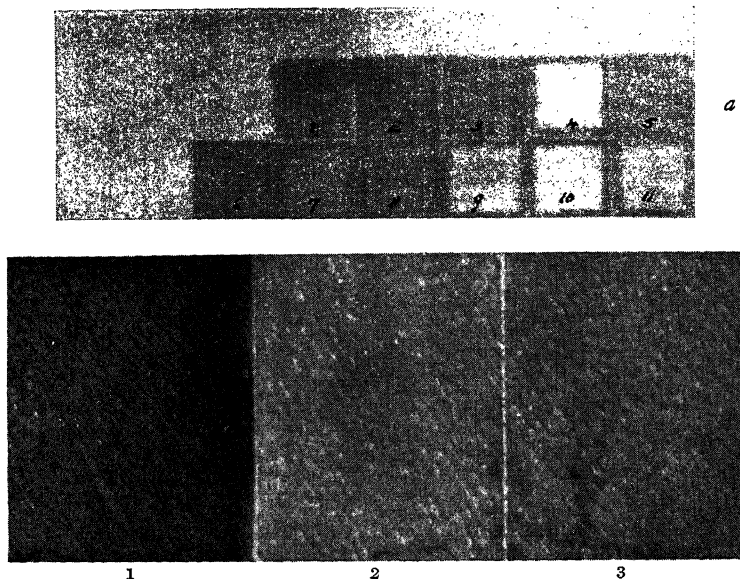
FIGURE 70. *a*,—Yellowing produced in white paint by covering part of the surface with coloured glass filters and exposing to sunlight. Transmission (cm.x10^{-5}): 1,—red celluloid; 2,—red filter, 600 up; 3,—red filter, 600 up; 4,—pink filter, 400-460, 550 up; 5,—orange filter, 560 up; 6,—deep yellow, 535 up; 7,—light yellow, 605 up; 8,—deep green, 500-570; 9,—light green, 400 up; 10,—deep blue, 410-510; 11,—very pale yellow, 400-500, dim, 500 up, bright. *b*,—Bleaching of yellow film by light. 1,—covered for two years; 2,—same as (1) but bleached by light within four days' exposure to daylight; 3,—portion left exposed to light during the entire period.

distilled pilchard oil also is free from this defect; heat-polymerized oils possess it to a lesser degree than raw oils, but air-blown oils are particularly prone to turn yellow. In general, it may be said that the greater the amount of polymerization given a fish oil prior to its use in a paint or varnish, the less is the tendency towards yellowing.

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(vii) EXPERIMENTAL WORK WITH FISH-OIL PAINTS

Considerable work has been done in these laboratories by Dr. O. F. Denstedt and the writer on the weathering properties of pilchard-oil paints. The accumulated data of four years' work on the properties of more than 100 different paints subjected to three types of weathering agencies are too extensive to include here in any great detail. A summary of the experiments with data concerning a few selected samples are therefore given.

TABLE LIV. Composition of experimental pilchard-oil paints

Paint no.	White lead	Zinc oxide	Leaded zinc	Other pigments	Driers	Oil		Remarks
1	(paint made in commercial plant)					Slightly bodied pilchard		
2	(paint made in commercial plant)					Slightly bodied pilchard linseed	50 50	
3	(paint made in commercial plant)					Linseed		
18.2	30		30		Manganese	Pilchard	40	Equal parts of SO₂ treated raw oil and SO₂ treated bodied oil mixed and ground with pigment
19.1	30		30		Cobalt	Pilchard	40	
24.1	30		30		Cobalt	Pilchard linseed	20 20	Oils mixed and given slight body at 250°C.
25.1	30		30		Cobalt	Pilchard	40	SO₂ treated oil washed with aq. sodium carbonate
28.1	30		30		Cobalt	Pilchard tung	32 8	Mixture bodied at 200°C. for 24 hrs. in vacuo
29.2	30		30		Cobalt	Raw pilchard bodied pilchard-tung mixt.	30 10	Bodied mixture same as 28.1
30.1	30		30		Cobalt	Pilchard tung	32 8	Used bodied decolorized pilchard and raw tung oil
33.2	30		30		Manganese	Pilchard	40	Pilchard bodied in vacuo at 200°C. for 30 hrs. with addition of 0.2% CaO
48.1	30		20	Titanium oxide 10	Cobalt	Pilchard	40	
6.2				Red oxide 50	Manganese	Pilchard	50	Raw oil. Cedar panel
7.2				Red oxide 50	Manganese	Linseed	50	Raw oil. Cedar panel
65				Red oxide 50	Cobalt	Pilchard	50	Pilchard pastes diluted with bodied oil. Metal panel

In the preparation of the experimental paints for the exposure tests, the following variables were studied: driers, treatment of the oil, and pigments. A few paints were made containing lead, cerium, copper, iron, nickel, aluminium, calcium, cadmium, mercury, zinc, tin, antimony and vanadium as driers. The majority of the paints, however, contained cobalt or manganese linoleates as the drying catalysts. Lead or cerium was used in conjunction with cobalt or man-

Paint no.	Days exposure	Protect-ivity	Remarks	Days exposure	Protect-ivity	Remarks
1	220	97	Cracking and scaling	400	88	Coarse scaling and cracking
2	220	99	Fine alligatored checks	400	97	Checking and cracking
3	220	99	Coarse alligatored checks	400	98	Checking; no cracks
18.2	103	45		283	15	Scaling
19.1	103	95		283	92	Scaling W.N.S.E.
24.1	94	99		274	99	Scaling; equal in all exposures
25.1	94	100	Fine alligatored checks	274	98	Coarse alligatored checks
28.1	94	90		274	88	Flaking in large flakes
29.2	94	100	....	274	99	....
30.1	94	100	Blistered	274	100	Blistered extensively
33.2	178	100	Perfect	219	100	Very slight checking
48.1	178	100	Perfect	219	100	Dull and rough
6.2	57	100	Blisters	172	100	Blisters practically collapsed
7.2	57	100	Perfect	172	100	Perfect but dull
65	381	100	Perfect but dull	730	100	Perfect but dirty

ganese driers in a few cases. The oils used included decolorized refrigerated oil, oils bodied by heat in air, in inert gases, and *in vacuo* at 200° (392°F.) and 250°C. (482°F.), mixtures of pilchard, linseed and tung oils bodied alone or as mixtures, steam-distilled pilchard oils, air-blown oils and sulphur-dioxide-treated raw and bodied oils. The pigment mixtures were relatively simple and included white lead, zinc oxide, leaded zinc, titanium oxide, barytes and lithopone. For coloured

pigments burnt umber, red iron oxide, chrome yellow and chrome green were used. Fillers included calcium carbonate and silica.

Exposures were made on an outdoor paint fence situated about 200 yards from Prince Rupert harbour and about 50 feet above sea level. In addition, exposures were also made on two types of artificial accelerated-weather devices. In one machine the painted panels were exposed to

as to protectivity (per cent of surface retaining its coating)

Paint no.	Days exposure	Protect- ivity	Remarks	Days exposure	Protect- ivity	Remarks
1	750	66	Severe scaling	1187	36	
2	750	60	Severe scaling	1187	25	
3	750	78	Scaling	1187	52	
18.2	633	2	W. exposure only one with film on			
19.1	633	22	Scaling. N.W.S.E.			
24.1	624	60	Scaling. Panels equal at all exposures	1061	5	
25.1	624	15	Scaling. Panels equal at all exposures	1061	5	
28.1	624	40		1061	20	
29.2	624			1061	5	
30.1	624	100(?)	Only first coat off	1061	82	
33.2	598	75	Cracked and scaled	960	10	
48.1	598	90	Minute cracks. Good ad- hesion	960	80	
6.2	702	100	Surface very dull	1478	100	Intact but dull
7.2	702	100	Perfect but dull	1478	95	Some peeling
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the light and heat (40°C.) from a bank of Mazda lamps for 4.5 minutes, ultraviolet light from a quartz mercury arc for 3 minutes, moisture in the form of a light spray for 9 minutes and finally a low temperature (-20°C., -4°F.) for 6 minutes. The exposures were automatic and continuous in the order named. The second artificial weathering device was manually operated and had for its object the determination of the type of weathering cycle most destructive to paint

29·2S   30·1S   28·1S

29·2W   30·1W   28·1W

29·2N   30·1N   28·1N

29·2E   30·1E

19·1E   18·2E   24·1N

19·1W   18·2W   24·1W

48·1E   25·1E   33·2E
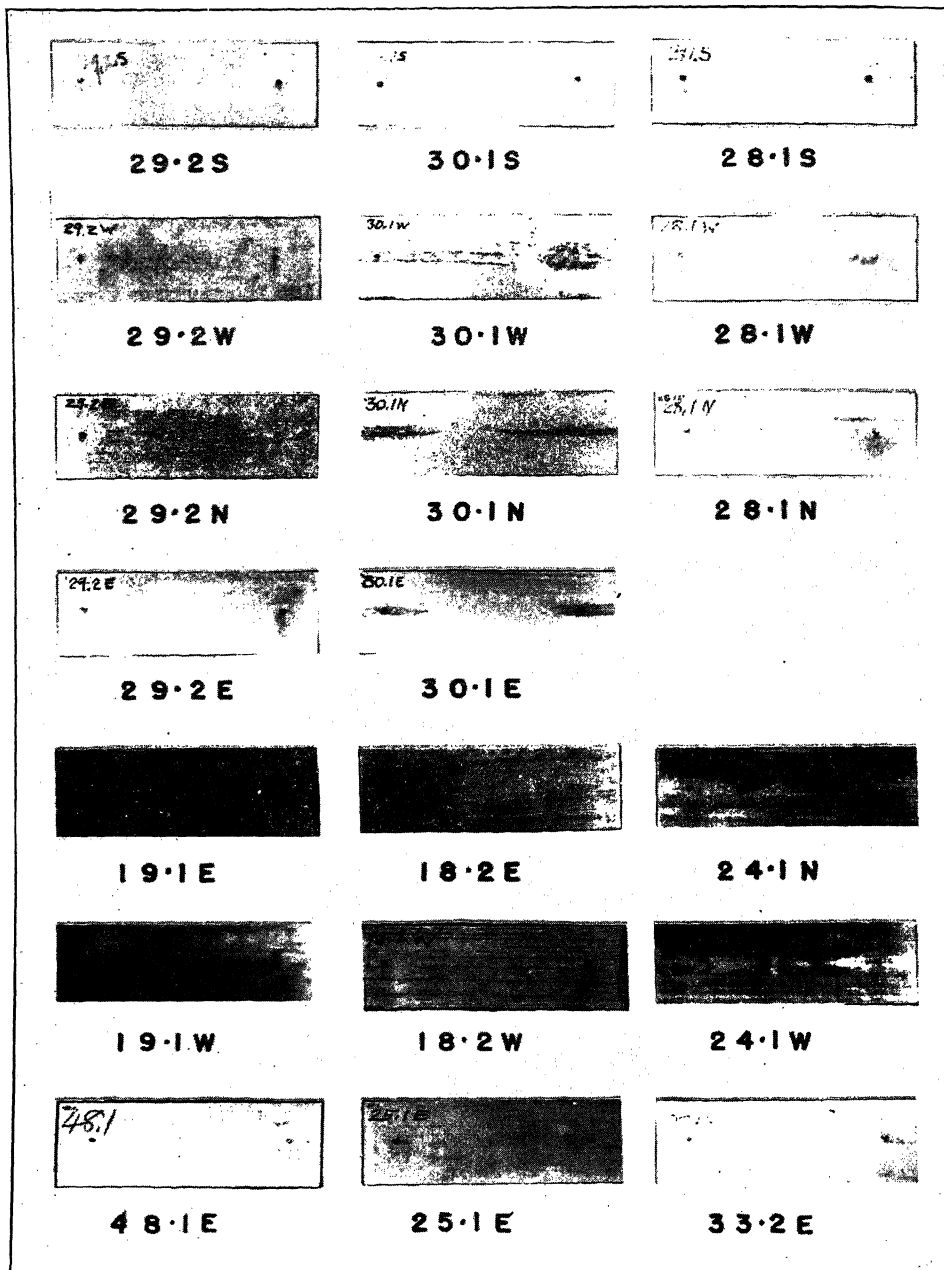
FIGURE 71. Panels weathered out-doors for three years.

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films. Various areas of the films were exposed for 24 hours to heat and light from a bank of Mazda lamps, ultraviolet light from a quartz mercury arc and moisture-saturated air at 40°C.

In table LIV are given the compositions of 15 experimental paints. These have been chosen to illustrate the effects of various factors, such as the use of mixed oils, heat treatment, etc. The results of outdoor exposure tests on these paints are set forth in table LV. The various coatings were evaluated on the basis of protection offered against weathering of wood surface after coating had failed. This was done by estimating the fraction of total panel surface that retained its coating. The chief type of failure was also noted. In figure 71 is shown the condition of some of the panels after 3 years' exposure and in figure 72 are shown some photomicrographs that elucidate the nature of the particular type of failure taking place in the films. These outdoor exposure tests were made on cedar panels which had received three coats of the experimental paints. The following observations are based on exposure tests of some 100 different paints.
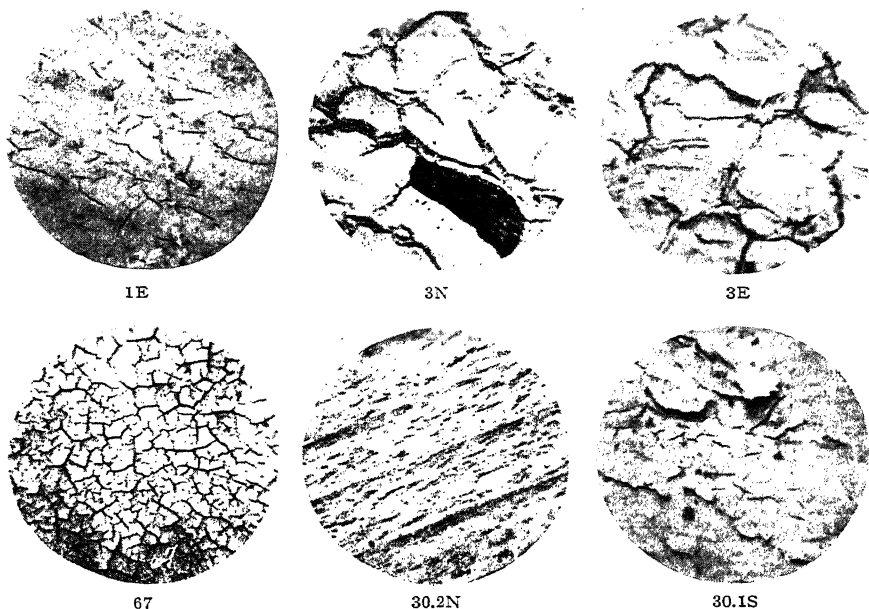
FIGURE 72. Type of failure in panels weathered out-doors.

In the freshly prepared panels tackiness was least evident with "tungate" driers; cobalt and manganese linoleates gave films less tacky than those produced by the same metals used as the soaps of pilchard-oil fatty acids. Tungate driers, however, gave dull films and for this reason the linoleates were preferred. Naphthenates showed no particular merits over the linoleates in preventing tackiness. Yellowing, as in the oil films themselves, was greatest in tung-oil combinations, less in pilchard-oil and least in linseed-oil paints. Yellowing was in all cases accompanied by a decrease in hardness. Year-old, non-exposed panels when subjected to tests showed hardnesses decreasing in the following order: commercial linseed oil, pilchard-tung-oil mixtures, pilchard-linseed-oil mixtures, bodied pilchard oil and raw pilchard oil.

Figure 73(A) shows the condition of panels of paints nos. 1, 2, and 3 after a four-year exposure in each of four directions. Paint no. 2, which contained a 1:1 mixture of linseed and pilchard oil, was definitely inferior to either the total pilchard- or total linseed-oil paint. It must be emphas-

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ized that this was the only case where a mixture of linseed with pilchard decreased the durability. In all other cases the use of linseed- in pilchard-oil paints increased the weathering properties of the latter paints. Figure 73(B) shows the effect of immersing panels painted with paints 1, 2 and 3 in distilled water for 1 week. All paints were intact but no. 1 was easily scraped off with the finger, no. 2 less easily and no. 3 only with difficulty. On drying again the panels recovered their original hardness and adhesion.
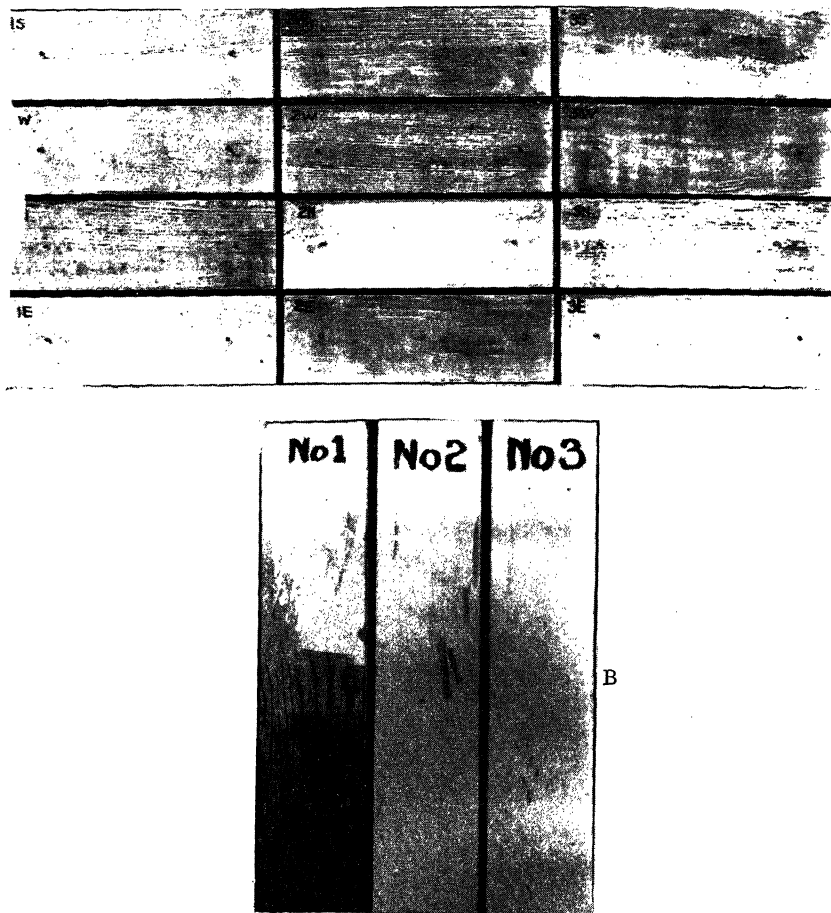
FIGURE 73. Comparison of linseed- (1), linseed-pilchard-(2), and pilchard-oil (3) paints. (A) After 4 years' exposure out-doors. (B) After immersion in water for 1 week.

The effect of processing pilchard oil before use in paints was in most cases clearly defined. Paints containing alkali-refined *and* decolorized pilchard oil broke down earlier than those containing oil simply decolorized, whilst those containing oil bodied at 200°C. were more durable than those with oil bodied at 250°C. Paints made with sulphur-dioxide-treated oil broke down very rapidly, particularly if the excess of sulphur dioxide was not removed. Oils treated with

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sulphur dioxide prior to heat-bodying produced less durable paints than those bodied before sulphur dioxide treatment. Clear varnishes made with steam-distilled pilchard oil were as durable as commercial varnishes. Enamels made with this product also had extremely good weathering properties. Adhesiveness of the film was an outstanding characteristic of varnishes and enamels made with the steam-distilled oil.

Better adhesive and cohesive properties in the dry paint film were obtained if, in the use of mixtures of oils, these were given a slight initial heat treatment. This heat treatment need not be extensive; a simple flash heating to 300°C. (572°F.) followed by rapid cooling is sufficient. For ordinary bodying of mixtures temperatures between 200° and 250°C. are, however, preferable. This preliminary heat treatment was especially necessary for pilchard-tung-oil mixtures, which, in general, made very durable paints. The durability of these mixtures was better when the proportion of tung oil was kept low, i.e. from 5 to 10 per cent; higher amounts caused some blistering and non-cohesion between the second and third coats.

The effect of pigments in pilchard oil paints was much the same as those in paints made with linseed oil. Zinc oxide tended to harden the film but reduced durability by causing a brittleness. Partial substitution of titanium oxide for zinc oxide in white-lead paints increased the durability considerably. White lead gave softer, more durable films but in the case of pilchard-oil paints they were so soft that they became dirty very quickly. Pilchard-oil paints with barytes tended to blister during the initial weathering exposure and finally became brittle and cracked. Lithopone pilchard-oil paints blistered and failed through poor intercoat adhesion. With bodied pilchard oil these defects were partly eliminated but were accentuated with sulphur-dioxide-treated oils. As with linseed-oil paints, coloured pigments prevented the films from drying hard until exposed for a considerable time; the darker the pigment the softer and tackier were the films.

The results of the artificial-weathering tests showed that ultraviolet light was the most active agency in causing breakdown in the paint panels. The effect of ultraviolet light was particularly noticeable when preceded by exposure to moisture. Although artificial weathering did not in all cases parallel the outdoor exposure tests, nevertheless, those paints that stood up best on the outdoor exposure fence also gave the best results during artificial weathering. This was especially true of those paints containing pilchard oil heat-bodied with a small amount of tung oil.

(e) FLOOR COVERINGS, OIL CLOTH, WATERPROOF FABRICS AND PATENT LEATHER

The application of drying oils to fabrics in the manufacture of floor coverings, oil cloth and various decorative and water-proof materials is a specialized branch of the paint and varnish industry and many of the properties of drying and semi-drying oils that are well known to paint and varnish technologists are also of importance to manufacturers of linoleum and other oil-coated fabrics. The inherent properties of fish oils that give elasticity to paint films are of some value in the manufacture of flexible oil-coated fabrics, but the softness and tackiness of these films also restrict their general use in this field. Certain kinds of processing increase their utility, but of course raise the cost to the manufacturer. Since the manufacture of oil-coated fabrics is more of an art than a science, it is not to be wondered at that some manufacturers claim to be able to use drying fish oils such as menhaden, sardine and pilchard to advantage, whereas other manufacturers have been unable to do so. It is certain, however, that in countries where linseed and other drying vegetable oils are scarce, fish oils and whale oils have been processed in ways which make them suitable materials for the production of linoleum, oil cloth, etc.

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(i) FELT-BASE FLOOR COVERINGS

These consist essentially of a fibre felt made of wood pulp, rag waste, etc., which is saturated with bitumen. By varying the bitumen mix, such as by the addition of Gilsonite, softer or harder felts can be produced. The remaining stages in the manufacture consist in covering the back and front with suitable decorative paints. A cheap quick-drying paint is sufficient for the back, but the upper face is treated very carefully. A sealing coat of paint is first applied to prevent bleeding of the bitumen saturant after which the pattern is printed on. Finally a coat of varnish is applied. In the manufacture of this type of covering, wintered fish oils such as menhaden, sardine and pilchard are used extensively in the priming coats. These oils are usually used in conjunction with tung, linseed and perilla oils, the blend with the first oil being in general more satisfactory than with the two other oils. The trade prefers a thoroughly wintered fish oil for this purpose but the presence of stearine is not so serious a drawback as it is in the paint and varnish trade.

(ii) LINOLEUMS

These are made by pressing a linoleum "cement" on to canvas or coarse jute fabric called the "hessian". The components of the cement and the method of its manufacture are the deciding factors in the quality of the resulting product. The starting point in the production of linoleum cement is the formation of a linoxyn made by the oxidation of a drying oil by one of the methods described in Section 8 of this Bulletin. The oxidized oil is then mixed with rosin and kauri gum and heated in a kettle until the gums are thoroughly incorporated. Heating at 110° to 130°C. (230° to 266°F.) is continued until the mass has a dry spongy appearance, after which it is cooled and stored until required for use. The cement is now pulverized and mixed with various proportions of powdered cork, wood meal and pigment, after which it is pressed on to the hessian. The material is then passed into drying or curing chambers where it is hung up and subjected to heat. After thorough maturing the linoleum is given a coat of cheap quick-drying paint on the back of the hessian and printed on the upper surface with a durable hard paint.

The linoxyn for linoleum cement is made chiefly from linseed, tung, perilla and soya-bean oils; fish oils are used to a certain extent, particularly where a slow-drying linoxyn is required. The chief drawbacks to the use of a raw or refrigerated fish oil in the manufacture of the linoxyn are the longer time required for the oxidation process (by the use of proper driers pilchard-oil films can be made to dry as fast if not faster than linseed-oil films) and the softer, stickier nature of the oxidized product. The latter defect can be overcome to a certain extent by blending with tung oil or by proper use of gums.

Another method described by Fritz (1938) is to blend oxidized fish or whale oils with linseed linoxyn. A method of oxidizing whale or fish oil suggested by Fritz is to moisten a layer (10 cm.) of linseed linoxyn with a blown fish oil and to allow it to dry in a room maintained at about 50°C. (122°F.) with periodic mixing. After drying, the process is repeated with the addition of a fresh lot of oxidized fish oil. After about ten additions of fish oil the fish-oil linoxyn can be used in

the manufacture of the linoleum cement. The fish-oil linoxyn then contains about 50 per cent linseed and 50 per cent fish oil. It is blended in a cement pan with the following ingredients: fish-oil linoxyn 330 parts, linseed linoxyn 670 parts, rosin 180 parts and kauri gum 65 parts. Cooking is continued until the desired consistency has been attained and the mass is dry and spongy. In making the actual linoleum 20 parts of this cement is mixed with 25 parts of cork meal and 8 parts of ochre. The final product is said to be entirely satisfactory. Sardine oil is considered to be superior to whale oil for this purpose and the Haco brands of fish oil, which are made from sardine oil, are also said to give a good product.

U.S. patent 2,050,646 describes a method for making a linoxyn that appears to be suitable for pilchard and other drying fish oils. A mixture of three parts of the oil with one part of rosin is heated until the gum dissolves, when 0.04 per cent of cobalt drier is added and the mixture blown with air at a temperature of 180°F. for 20 to 30 hours or until a sample just fails to dissolve in ethyl ether. The blowing is then discontinued and the non-oxidized portions of the oil dissolved out with petroleum spirits or petroleum naphtha. The undissolved portion is heated to drive off the solvent and then dissolved in a suitable solvent such as xylene, butyl acetate or high-flash-point coal-tar naphtha to give a solution containing 60 to 80 per cent of the oil. Rosin-ester gum, kauri gum, paracoumorone resin or oil-soluble phenol-aldehyde resins may be added to the solution or to the oil prior to oxidation. For making the moulding composition, 25 to 50 parts of the resin solution is added to 25 to 35 parts of vegetable fillers and 25 to 40 parts of mineral fillers.

Other methods of preparing fish oils for use in making linoxyn involve the distillation of the oil to remove the saturated components. Kaempfe (1935) distils the fatty acids of whale oil and obtains a polymerized residue which he claims can be utilized in linoleum manufacture. The steam distillation process described by Denstedt and Brocklesby (1936b) can also be used for this purpose. If the distillation is stopped before the polymer turns rubbery, the thick oil can be blown with air. The product forms a stiff rubbery mass, extremely sticky until exposed to the air for some time. If the blowing is not carried too far, the product can be fused with gums to form a satisfactory cement to bind wood meal and the like.

(iii) FLOORCLOTH

This is a coarse jute or canvas backing that has been given several thick coats of paint. The base coats consist of whiting and/or china clay mixed with linseed oil as a binder. The final coats are hard decorative paints and varnishes. The back of the jute or canvas is also given a thin coat of paint. The base coats are spread on the canvas by mechanical spreaders. The fillers, whiting or clay, are first mixed into a thin paste with water, after which the desired amount of linseed or other drying oil is added and the whole run through a grinder to eliminate any gritty particles that may be present. The cloth spread with the wet paste is run into a drying room maintained at a temperature of from 130° to 170°F. After thorough drying several other coats may be applied, whereupon the material is ready for the final application of the decorative paint. Much of the quality of the floorcloth depends upon the nature and mode of application of the filling coat. Pliability is one essential and it is here that certain fish-oil combinations are used to advantage. As in the manufacture of felt-base coverings, the fish oil is usually blended with linseed, perilla or tung oil, the amount of fish oil and nature of the vegetable oil depending upon the particular characteristics required by the manufacturer.

(iv) OIL CLOTH

This is made in practically the same manner as floorcloth with the exceptions that a cotton cloth is used for the fabric, thinner coatings of filler are used and

greater smoothness and gloss on the surface are required. In addition there is need for more flexibility than is necessary in floor coatings. This flexibility can be attained by the use of certain proportions of fish oils in the paints or varnishes and for this purpose the residual polymer obtained by steam-distilling pilchard oil is very suitable.

(v) PATENT AND ENAMELLED LEATHERS

These are made by applying special enamels to prepared leather. The enamels usually consist of polymerized boiled linseed oil containing suitable driers such as lead, manganese, Prussian blue and suitable pigments. As a rule three coats are applied, each being dried under special conditions. After the third coat is dry, the product is exposed to the sun or ultraviolet light for several hours to make the coating more flexible. The use of refrigerated drying fish oils in enamelled coatings has been found to be satisfactory with the exception of a tendency for the coating to bloom. This bloom is easily removed by polishing. Enamels made from steam-distilled pilchard oil are practically free from this defect.

(vi) OILED SILKS AND LINENS

These are simply made by coating the fabrics with raw or boiled drying oils. Products made from drying fish oils show many superior qualities over those made with linseed oil. They are more flexible and less prone to crack. They possess no fish-oil odour and dry to give a practically non-tacky film. Those products made with a refrigerated pilchard oil with no drier added appear to possess better weathering properties than those containing slight amounts of cobalt or manganese driers although the use of such driers permits faster initial drying. Samples of oiled fabrics prepared in these laboratories from pilchard and linseed oils have been examined over a period of five years. Fabrics oiled with linseed oil became brittle after a period of about one year and would stand but little handling without cracking. A sample of silk oiled with refrigerated pilchard oil without driers was still soft and pliable after a period of five years. A similar sample containing a small amount of cobalt drier was slightly discoloured and more brittle than the one without drier.

(f) CORE OILS

Sand cores are used for forming the cavities in iron or steel castings, as for instance the hollow sections of steam or hot-water radiators. The core is set in the sand mould and the molten metal run in between them to form the shell. Although many types of cores are used, sand cores find the widest application. These cores consist of sharp-grained sand mixed with a drying or semi-drying oil. The mixture is moulded in a wooden pattern and baked in an oven to oxidize the oil which dries through polymerization and oxidation to bind the sand particles together into a solid mass. The sand is usually dampened with about 6 per cent of water to facilitate mixing of the oil. A water-soluble binder such as casein or dextrin is also used to impart some strength to the core before it is

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baked. The baking of the core simulates in many respects the baking of oil-varnish films and an oil or mixture of oils that gives a firm hard baked varnish film will usually be found satisfactory for core-oil manufacture. Linseed oil has for many years been recognized as the standard material for cores, but recently other oils have been investigated. Chief among these are perilla, bean, corn and certain fish oils. The annual consumption of core oils in Canada is about 250,000 gallons.

Core manufacture is not standardized and consequently each foundry has its own ideas as to what constitutes a satisfactory core, but in general the following characteristics are desirable. The core should have mechanical strength. Transverse strength when measured by breaking a bar 1 inch square and 8 inches long supported on 6 inch centres should be from 25 to 50 pounds per square inch. Tensile strength as measured on a standard cement tester should run from 150 to 225 pounds per square inch. It is claimed that low permeability in sand cores gives a better finish to the casting. In practice the cores are sufficiently vented to the outside to permit egress of gases, but a certain permeability is required to allow the gases to reach the vents and thus prevent the formation of gas pockets. Finally, although the time required for baking is not of paramount importance, a quick-baking core allows faster production and a certain saving in heat requirements.

Although linseed oil has been used for the base of core oils for many years, efforts to reduce the cost of such core oils have resulted in mixtures of linseed with other vegetable oils, rosins and mineral oils being marketed. Raw soya-bean oil mixed with linseed oil gives cores equal in strength to those produced with straight linseed oil, but they require longer baking times. A satisfactory core oil is made according to U.S. patent 1,822,411 by reacting rosin glycerol ester with a semi-drying oil with an iodine value of 100 or over at a temperature between 260° and 305°C. (500° and 580°F.). Glycerol esters of the highly unsaturated fatty acids of fish oils (Armour and Company's Neo-fat no. 19) are also recommended as a core oil. The specifications of two commercial core oils containing linseed and mineral oil are given as follows:

	Sample A	Sample B
Iodine value..........	192	154
Saponification value....	115	115
Acid value............	22.7	29.2

Tensile strength: 60 parts sharp sand to 1 part oil by volume, baked at 205°C. (400°F.), sand containing 6 per cent moisture.

45 minutes..........	126	129
90 "	187	193
150 "	212	209

From these data it will be seen that there is no relationship between the unsaturation of the core oil and the tensile strength of the resultant cores. Both materials give increased tensile strengths with increased time of baking.

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Since it is possible to produce hard films by baking pilchard oil films, it is reasonable to suppose that pilchard oil would be a suitable oil for core making. Also, since raw pilchard oil films are softer than those of linseed oil, it might be expected that this characteristic would be reflected in the nature of pilchard-oil sand cores. Experimental work done in these and other laboratories fully confirm these expectations. Mr. S. M. Robinson of F. Hyde and Co., Montreal, has kindly permitted the writer to quote some data obtained on the use of pilchard oil in sand cores, given in table LVI. In this work 45 parts of sand was thoroughly mixed with 1 part by weight of the oil and the cores baked at 205° to 230°C. (400° to 450°F.). Mr. Robinson considers these values quite satisfactory. He has also obtained excellent results by the use of mixtures containing 50 per cent of linseed oil and 50 per cent of a raw pilchard oil containing a small amount of non-crystallizing rosin.

TABLE LVI. Strengths (pounds per square inch) of pilchard-oil sand cores
(Courtesy of F. Hyde and Co., Montreal)

Treatment of oil	Tensile strength	Transverse strength
Raw linseed oil	250	85
Pilchard oil heated 2 hours at 300°F., 5% dextrine added at 150°F.	265–300	75–75
Pilchard oil heated at 450°F. with 2%PbO	385	105
Pilchard oil heated at 520°F. with 1% MnO_2	200	65

In these laboratories a large number of core mixtures have been made using linseed, perilla and pilchard oils. In preliminary work it was found that the best results were obtained by firing the cores in an electric oven fitted with a circulating fan and at a temperature of 200° to 205°C.

TABLE LVII. Tensile strengths (pounds per square inch) of cores made with various oils and baked at 200° to 205°C.

Kind of oil and treatment	After baking for		
	60 min.	90 min.	120 min.
Commercial core-oil mixture	18	18	..
Raw linseed	113	115	90
Raw linseed plus 1% Co	108	106	90
Raw linseed plus ½% Mn	98	121	114
Raw perilla	116	116	77
Raw perilla plus 1% Co	112	104	81
Raw pilchard	65	57	49
Raw pilchard plus 1% Co	63	75	62
Raw pilchard plus 1% Pb	79	79	73
Raw pilchard plus ½% Mn	86	97	93
Oil mix: 165 pilchard, 15 rosin, 10 mineral, 10 corn starch, 1 lead oxide by weight.			
1:32 by volume	76	110	100
1:24 by volume	147	185	165

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(390° to 400°F.). The data given in table LVII were obtained by using the oils in the proportion of 1 to 45 of sand, the latter containing 6 per cent water. Well washed sea sand was used which was made up of the following particle sizes: over 40 mesh, 42.7 per cent; 40 mesh, 53.2 per cent; 60 mesh, 3.2 per cent, and over 60 mesh, 0.9 per cent.

The tensile strengths given by these cores are much lower than usually obtained in commercial practice and it is probable that the type of sand used had some influence on the results. However, in all cases pilchard oil gave lower tensile strengths than those of either linseed or perilla oils. Increasing the amount of oil, as shown in the oil-mix data, increased the tensile strength of the cores. All of the above cores, however, had similar porosities and friabilities. A series of cores was made up and baked by a local foundry with oils supplied by these laboratories. An average of ten cores showed tensile strengths of 75 pounds per square inch for raw linseed and 82 pounds for raw pilchard plus 1 per cent cobalt. The foundryman expressed complete satisfaction with both series of cores.

In a second series of experiments cores were made up with a Belgian silica sand which had the following composition: over 40 mesh, 31.1 per cent; 40 mesh, 42.9 per cent; 60 mesh, 18.5 per cent; over 60 mesh, 7.5 per cent. Eight to 10 cores were made up with each oil using 1 part of oil to 45 parts by volume of sand, the latter containing 6 per cent moisture. The data in table LVIII were obtained.

TABLE LVIII. Tensile strength (pounds per square inch) of cores made with Belgian sand and various oils

Kind of oil and treatment	After baking for	
	60 min.	90 min.
Raw pilchard......................	56	111
Cold cleared pilchard (heavy pressed)	85	137
Raw pilchard plus 0.1% Co........	90	118
Raw pilchard plus 1% Pb.........	113	109
Blown pilchard plus 0.1 Co.........	87	93
Polymerized pilchard plus 0.1% Co..		76
Raw linseed......................	172	201
Linseed plus 0.1% Co.............	149	126
Linseed plus 1.0% Pb.............	144	121
Raw perilla......................	184	180
Perilla plus 0.1% Co.............	158	101
Perilla plus 1.0% Pb.............	200	141

Again all the pilchard-oil cores were lower in tensile strength than either linseed or perilla. The heavy pressed pilchard-oil cores baked for 90 minutes were pronounced very satisfactory by a practical foundryman. Cores with raw pilchard having 1 per cent lead were also fairly satisfactory.

A final series of cores was made with the Belgian sand in which 85 parts of an oil mixture was blended by heating with 10 parts of resin, 5 parts of casein and 1 part of lead oxide. Oil mixture no. 1 contained 1 part of linseed and 3 parts of raw pilchard; mixture no. 2 contained equal parts linseed and raw pilchard; and mixture no. 3 contained 3 parts of linseed to 1 of pilchard. The cores were made up and baked under conditions the same as just described. Transverse- and rupture-resistance measurements were kindly made by Mr. S. M. Robinson of the F. Hyde and Co., Montreal. The results are given in table LIX.

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TABLE LIX. Strengths (pounds per square inch) of cores made with Belgian sand and pilchard-linseed-oil mixtures

Oil mixture	Tensile strength after baking for		Transverse strength after baking for		Rupture resistance after baking for	
	60 min.	90 min.	60 min.	90 min.	60 min.	90 min.
No. 1 Linseed-pilchard ratio 1:3..........	155	106	53	51	160	123
No. 2 Linseed-pilchard ratio 1:1..........	193	193	51	55	145	178
No. 3 Linseed-pilchard ratio 3:1..........	218	175	55	52	182	154

Considerable variations were found in these cores, particularly in the measurement of the rupture resistance. In general, however, it can be stated that increasing the amount of linseed oil in the mixture increased the tensile strength, but had not much effect on either the transverse strength or resistance to rupture. Good cores should have tensile strengths of not less than 200, transverse not less than 65 (some authors state that from 25 to 50 is satisfactory) and in the rupture test should stand 200 pounds for 60 seconds. None of the above cores gave such figures.

These experiments are not to be taken as conclusive. Baked pilchard-oil films can be made as hard and strong as linseed films and it should be possible to get cores of satisfactory strength when made with this oil. The fact that factory-made cores containing pilchard oil are as strong as linseed cores made up with the same sand and baked under similar conditions shows that the baking technique is of some importance. Also it has been suggested that pilchard oil should be mixed with the sand at temperatures slightly higher than room temperature. Finally, it should be remembered that tensile- and transverse-strength measurements are not the only criteria of judging satisfactory cores. Many of the pilchard-oil cores made during these experiments were judged to be satisfactory by practical core makers. Cores that are too hard are sometimes difficult to remove from the casting. Given a certain degree of hardness, the practical core maker seems to be more interested in the permeability and friability. The latter characteristic determines the resistance to crumbling and therefore the retention of sharp edges. In this respect pilchard-oil cores were as satisfactory as either linseed- or perilla-oil cores.

(g) PRINTING INKS.

Printing inks consist essentially of a pigment ground in an oily vehicle. A specially treated drying oil such as linseed oil very commonly forms the base of such a vehicle, which contains, in addition, materials such as rosin, rosin oil, a fat or rosin soap drier, and sometimes mineral oil. Besides linseed oil, other vegetable drying oils such as tung are used, and drying fish oils

have received considerable attention as evidenced by the increase in the United States factory consumption of fish oils for printing-ink purposes, which rose from 103,000 pounds in 1934 to 254,000 pounds in 1938. Corresponding data for Canadian usage are not available.

Depending on the nature of the printing process used (web press, flat bed, engravure, rotogravure, lithography, etc.), the ink must have definite degrees of physical properties such as viscosity, tackiness, drying power and absorption, as well as compatability with the pigments employed. The securing of the proper combination of properties is a technological art and it is difficult to predict whether any given drying fish oil can be processed to acquire the necessary properties to allow it to serve as the base of the pigment vehicle. The linseed or fish oil is bodied by a partial polymerization and condensation brought about by heat. "Top-firing" is a common process involving heating the oil until volatile products are given off. These are ignited and allowed to burn until a drop of the oil no longer leaves a grease spot when placed upon paper. Such an oil tends to produce a "short" ink, i.e. one which adheres in the depressions of an engraved block when the excess ink is rubbed off with a rag before taking an impression. A second bodying process consists of heating the oil to about 300°C. (570°F.) in an open kettle but without igniting the volatile products given off. By varying the time of heating, a number of grades may be prepared which tend to produce a "long" ink, i.e. one which is tacky and transfers uniformly from the ink reservoir over the various rollers to the type.

Potassium, sodium, calcium, aluminium, and other metallic soaps, frequently incorporated in the ink to assist it to "lift" from the type on to the material to be printed, can be prepared from marine animal oils. The same also applies to certain driers (metallic soaps of drying fatty acids) that are added to promote the surface drying of the ink by oxidation simultaneously with its absorption by the printed material.

Herring, sardine, menhaden, whale, and British Columbia pilchard oils have been described as suitable for blending in various proportions with linseed and other vegetable oils during the manufacture of different kinds of printing inks. The marine oil is cold-cleared and sometimes further refined or treated before bodying, since the odour is objectionable in some inks. One process of refinement consists of heating the cold-cleared oil to 212°F. with 2.4 to 4.0 per cent of sodium bicarbonate and 0.8 to 2.4 per cent of alum in the form of an aqueous solution. The mixture is stirred continuously until most of the water has evaporated, and any stearine that later separates is removed. The simple bodying processes just mentioned as applied to vegetable and fish oils are frequently supplemented or replaced by special treatments. British patent 338,932 describes the heating of fish oils to 390°F. in the presence of various metals, metallic oxides, halides, halogens or inorganic acids to obtain products with properties similar to those of tung oil. Sardine or pilchard oil of iodine value about 174, after being bodied at 555° to 570°F. in a moderately high vacuum, is subjected to a very high vacuum process of molecular evaporation and the residue having an iodine value of about 104 is stated to have suitable characteristics as an ink vehicle.

A portion of the tung oil in a rapid-drying typographic ink vehicle may be replaced by fish oils that have been halogenated in the presence of an activator such as zinc and aluminium paste (U.S. patent 2,136,108). The speed of drying of the ink is stated to be proportional to the degree of halogenation. The drying power of the naturally-occurring glycerides in fish oils

intended for printing ink and other products may be enhanced by hydrolyzing the oils, separating the less unsaturated fatty acids from the more unsaturated acids by distillation, then re-esterifying these acids with glycerol or other polyhydroxic alcohols (British patent 477,207). Sulphated and sulphonated fish oils are in use as non-inflammable, innocuous inks for photogravure processes.

Whale oil has been used as a constituent of ribbon inks to suppress drying and spreading, and cetyl alcohol is suggested as a constituent of waxy ink compositions for carbon papers and typewriter ribbons (U.S. patent 2,135,735).

(h) RUBBER MANUFACTURE

In 1937 Canada imported over 3 million pounds of stearic acid worth approximately a quarter of a million dollars. During the same year the rubber industry consumed about 750,000 pounds of stearic acid or stearic-acid substitutes, most of which was imported. Recently, the manufacture of stearic-acid substitutes from Canadian fish oils has been undertaken by a Canadian firm and the domestic product appears to be meeting the approval of Canadian rubber manufacturers. It is therefore of some interest to consider properties of commercial stearic acid and its substitutes and the use of these substances in the rubber industry.

Commercial stearic acid is made chiefly from tallow. The tallow is split into its component parts, glycerine and fatty acids, by the use of a catalyst and medium-pressure steam. [The Twitchell process is commonly used (Section 8)]. The recovered fatty acids are chilled and pressed in a hydraulic press to remove the liquid acids from the solid. The solid mixture remaining in the press is the "stearic" acid of commerce. It consists chiefly of solid stearic acid, some liquid oleic acid and small amounts of other fatty acids. The proportion of stearic to oleic acid depends upon the number of times the mixture has been chilled and pressed. The single-pressed product consists of approximately 85 per cent stearic and 15 per cent oleic, whilst the double- and triple-pressed products contain approximately 90 and 95 per cent stearic acid. Each grade is melted and boiled with a small amount of sulphuric acid to improve the colour. After washing with hot water the free acids are drawn off and allowed to solidify in moulds. The product is marketed as slabs, powders, flakes or beads for the various trade requirements, the rubber industry preferring the flaked or beaded forms.

Probably the chief function of stearic acid in rubber compounding is a chemical one. During the vulcanization process accelerators are added to control the action of the sulphur on the rubber. These accelerators in nearly all cases are improved by the addition of zinc oxide, which to be effective must be dissolved in the rubber. Zinc oxide alone is not soluble, but, in the presence of stearic acid, zinc stearate is formed which readily passes into solution. Crude rubbers contain varying amounts of fatty acids and it has been found that the poorer grades are invariably deficient in their content of such acids. The addition of stearic acid may in some cases improve a crude rubber of poor quality to one of first grade. Stearic acid also acts as a softener and plasticizer and assists in the dispersion of the various materials that are added during the compounding processes. Whilst oleic acid is about equal in its effectiveness in the above functions, it has a marked tendency to "bloom" or migrate to the surface of the finished product, thus spoiling the appearance of the rubber and, in addition, greatly depreciating the physical properties of the product. For this reason rubber manufacturers are very particular about the content of oleic or other unsaturated fatty acids in the stearic acid they use. Single-pressed stearic acid is practically invariably used and a typical specification is as follows: melting point (minimum) 52°C., saponification value 208 to 212, acid value 207 to 210, iodine value (maximum) 10 to 12.

Stearic acid is not unique in its rubber-compounding properties. Other saturated fatty acids with fewer carbon atoms such as lauric, myristic and

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palmitic acids have been found to be satisfactory. Recently, fatty acids of higher carbon content have also been found to be efficient. As shown in Section 2 of this Bulletin, fish oils contain unsaturated fatty acids of high carbon content and when such acids are saturated with hydrogen so that the iodine value is 10 or less it has been found both experimentally and in practice that they are as efficient, pound for pound, as double-pressed stearic acid. Furthermore, the hydrogenation process enables one to produce a more saturated product of more uniform quality than is possible by the physical process of cold pressing. The lower content of unsaturated fatty acids favours the aging of the rubber with a lessened tendency to bloom. Consequently fatty acids from hydrogenated fish oils are recognized as standard materials for rubber processing.

TABLE LX. Characteristics of fatty acids from hydrogenated pilchard oils

Sample no.	Description	Titre (°C.)	Iodine value	Acid value	Saponification value
1	Hydrogenated acids from pilchard - oil stearine..........................	51.0	10.5	199.0	206.5
2	Hydrogenated acids from unrefined pilchard oil.........................	49.9	10.9	198.4	204.7
3	Hydrogenated acids from refined pilchard oil.............................	52.9	2.7	196.8	205.5
4	Commercial hydrogenated fish-oil fatty acids imported from U.S.A..........	53.2	1.4	189.1	200.8

Hydrogenated fish-oil fatty acids have been prepared in these laboratories and the products tested by the National Research Laboratories in Ottawa through the courtesy of Dr. G. S. Whitby. Table LX shows the characteristics of the samples tested. Commenting on the rubber-compounding tests made on these samples, the National Research Council reports: "It can be stated that Nos. 1 and 2 are slightly inferior and that 3 and 4 are about equal with the advantage, if any, in favour of number 3". The report states further as a conclusion: "All the samples of hydrogenated pilchard oil fatty acids submitted are satisfactory for use in rubber compounding, number 3 being the best and the one most likely to find acceptance by the rubber industry".

Canadian fish oils suitable for the manufacture of hydrogenated fatty acids for rubber manufacture include pilchard, herring, salmon and halibut head oils. All these oils are relatively low in unsaponifiable matter (usually less than 1 per cent) and when almost completely hydrogenated yield fatty acids with the titre points shown in table LXI. The relationship of titre to composition has already been discussed in Section 5. All of the above hydrogenated fatty acids meet the usual specifications demanded by the rubber industry in respect to

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unsaturation, titre point, unsaponifiable matter and saponification value. Chiefly due to its relatively low unsaturation British Columbia herring oil is at present being used to the greatest extent in this field.

TABLE LXI. Titres of fatty acids from hydrogenated fish oils

	Pilchard oil	Herring oil	Salmon oil	Halibut head oil
Iodine value............	1.6	3.4	1.4	3.2
Titre point (°C.)........	53.3	53.5	55.8	53.7

(*i*) SOAPS

As mentioned in Sections 5 and 8 the treatment of fats with alkali causes saponification or hydrolysis, with the formation of glycerol and the alkali salts of the fatty acids. Only the salts of the higher fatty acids are classified as soaps, as they are the only ones that provide the particular colloidal properties in aqueous solution that are characteristic of soaps. The various methods used for the formation of soaps have already been treated in the Sections mentioned.

(i) DETERGENT ACTION

The sodium, potassium and ammonium soaps are most generally used in the preparation of soap products for use as detergents. These are the soluble soaps and the solubility increases in the order given. The solubility of soaps decreases with increasing molecular weight and increases with rising temperature. The sodium soaps of the higher fatty acids are solids while the potassium and ammonium soaps are soft and semi-liquid.

The salts of the lower members of the fatty acid series form true solutions and have no detergent properties and it is only when the solutions begin to show colloidal properties, which occurs at about C_{12}, that detergency begins to appear. As the number of carbon atoms increases, the solubility decreases and the detergent efficiency goes through a maximum for any given temperature. Under ordinary conditions this occurs at about C_{18}, and under ordinary washing conditions the C_{18} soaps form the best soap; sodium stearate is an excellent detergent, but sodium oleate, the salt of the mono-unsaturated acid, is even better and constitutes the soap *par excellence*.

The soaps of the higher fatty acids have still higher optimal temperatures for detergency and, while the C_{20} and C_{22} acids which occur in fish oils provide poor detergents at ordinary temperatures, at the higher temperatures of the steam laundry they are quite satisfactory.

Soaps prepared from fish oils are made up of components covering a wide range of carbon classes and unsaturation, hence they show detergency over a wide range of conditions. The main factors that have brought disfavour on fish-oil soaps have been their tendency toward rancidity and the development of fishy odours. This is due to the presence of the highly unsaturated acids

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which are extremely sensitive to oxidation. This may be overcome by reducing the unsaturation by hydrogenation, thus securing stabilization against oxidation. During the course of hydrogenation the detergent power of the fatty acids increases until all the highly unsaturated acids are converted into mono-unsaturated acids, but after that, continued hydrogenation decreases the detergency, probably due to the marked decrease in solubility. Unsaturation may also be decreased by heat polymerization of the oil.

The effects of hydrogenation, polymerization and combined polymerization and hydrogenation on detergency were studied in these laboratories (H. N. Brocklesby, W. A. Riddell and Norma I. Rogers, unpublished data) to determine whether satisfactory soaps could be prepared from the highly unsaturated fish oils by using polymerization methods.

Some investigators have used criteria such as surface tension, drop number, lather number, etc., as a means of evaluating soaps, but, since the value of the soap as a detergent must be interpreted from these data, it seemed advisable to apply washing tests directly.

Two types of wash machine were tried, one a wash wheel after the type designed by Morgan (1932) and the other a vertical plunger type. In the latter machine the test pieces of cloth were stretched on two parallel fingers mounted in such a way that duplicate samples could be plunged vertically through the soap solution while the cloth was maintained rigidly horizontal. This type gave the most concordant results though the cleaning was not as great as in the wash wheel, as there was no mechanical agitation.

The cloth chosen for the tests was Wabasso sheeting and the same material was used throughout. Various soil solutions were tried, each being made up in a base of carbon tetrachloride with carbon black, Nujol and a hardened fat. The method of applying the soiling solution to the cloth is described by Morgan.

The soap solutions were prepared by weighing out the requisite quantity of free fatty acids, prepared from the oils in the usual manner immediately prior to use, and adding them to water with sufficient alkali to bring the final solution to a pH of 10. The water and alkali were maintained at the washing temperature during the solution of the fatty acids, and a definite time was allowed between introducing the fatty acids into this mixture and beginning the wash. By these procedures close comparison between the alkali present and the pH was obtained throughout all washes.

The soiled samples of cloth were measured in a reflection photometer, using a photoelectric cell to measure the reflected light. The cell was of the same type as used in the Evelyn colorimeter and the readings were taken on a similar galvanometer. The readings were taken before and after washing and the efficiency of washing recorded in terms of difference of the L value.

There is little effect in varying the concentration of soap from 0.1 to 1.0 per cent, but beyond that there is a decrease in washing efficiency, and for these tests the concentration of 0.25 per cent was adopted. The temperature of washing similarly showed little difference from 25° to 40°C. (77° to 104°F.), with a marked decrease in efficiency above these temperatures when the soap from the mixed fatty acids of pilchard oil was used. Washing for varying lengths of time showed a preliminary rapid increase in whiteness up to 20 minutes and with longer washing a steady but slower whitening, and on the basis of this information a washing time of 30 minutes was adopted. These results are presented graphically in figure 74, a, b, and c.

The effect of hydrogenation on the detergent power of oils is to increase it until the highly unsaturated fatty acids have been reduced to the mono-

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unsaturated stage, after which the continuation of hardening decreases the solubility to such an extent that the soaps obtained are not as effective in washing. However, properly controlled hydrogenation of fish oils may be used to produce a soap stock which can be used to advantage, when blended with other oils, for the production of laundry soaps.
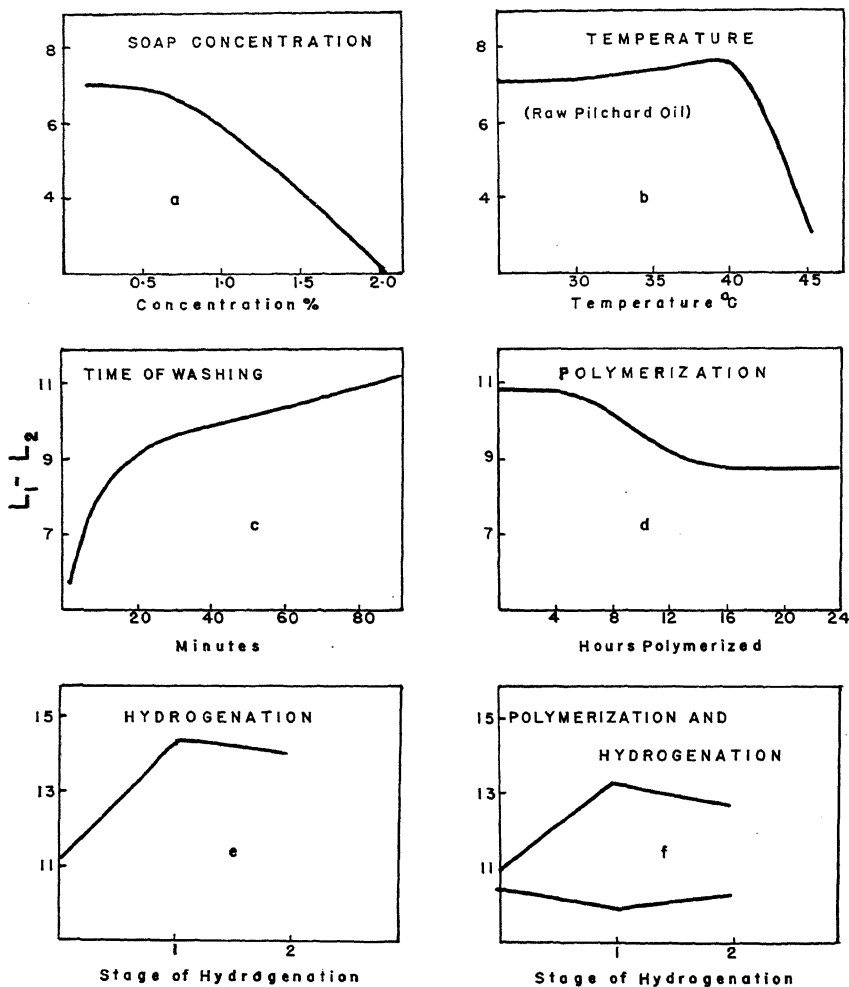
FIGURE 74. Washing efficiency (difference in L value) of pilchard oil soap under various conditions. L = 2-log. G = optical density, where G = galvanometer reading.

Polymerization decreases the detergent value of soaps produced from such an oil as compared with the raw oil, but there appears to be little difference in value as the polymerization is continued from 4 to 24 hours. The results of

washing with soaps prepared from pilchard oil polymerized for varying lengths of time are shown in figure 74d.

The effect of hydrogenation of the polymerized oils was studied and, while the results were not as conclusive as might be desired, there appeared to be little change in the value of the soaps as detergents. The results of these tests as well as those for the hydrogenation of raw pilchard oil are shown in figure 74e and f, where two stages of hydrogenation are indicated. The first stage was carried to the extent that all highly unsaturated acids should be removed, and the second stage was such that only monoethylenic bonds should remain in any fatty-acid residue.

The indications of this work are that soaps can be produced which have satisfactory detergent powers for ordinary use, by either hydrogenation alone or by polymerization followed by hydrogenation. By these processes the highly unsaturated acids that cause the recurrence of fishy odour in soaps are removed by saturating the double bonds, and a stable soap should result. Blending the treated oil with other oils has been shown by other workers (Knigge 1933, Ueno *et al.* 1933) to provide very satisfactory soaps.

The introduction of antioxidants to prevent rancidity has increased the stability of soap to a considerable extent and many individual compounds and types of compounds have been patented for this purpose.

Catalysis of oxidation due to traces of copper and iron from the boiling kettles has been largely eliminated by the application of nickel or stainless steel to the fabrication of the soap-boiling vessels.

It has been shown that the formation of nascent soap in the fibres, by first soaking the fabric in the fatty acid followed by treatment with alkali, produces cleansing many times greater than where preformed soaps are used for washing. It may be that the fatty acid penetrates the fibres of the textile better than a soap solution, or that the particles of grease and dirt are dissolved or wetted better by the fatty acid than they are by the soap solution, and are thus removed more effectively with the soap when it is formed. This procedure is used to a very limited extent in laundry practice.

(ii) USES OF METALLIC SOAPS

The use of soaps of such metals as lead, cobalt and manganese as driers in paint has been mentioned in the section dealing with oxidation. Lead oleate is used to some extent as the adhesive material in medicinal sticking plasters, while lead oleate and stearate are used in wax discs for sound recording.

Calcium soaps are well known in the production of cup greases and other lubricating greases, while barium soaps made up as a jelly with turpentine may be used as floor or boot polishes. The gel prevents the evaporation of the solvent and the mass remains soft for a considerable time.

Tin oleate formed on the fibres is used in connection with the dyeing of textiles. The fabric is treated with oleic acid and then with stannic chloride, causing the formation of tin oleate which acts as a varnish on the surface of the

fibres and thus gives greater depth and lustre to the colour. Tin linoleate has also been used as an antioxidant or resin-formation inhibitor for petroleum products.

Waterproofing of canvas, bricks and other building materials may be accomplished by the application of aluminium oleate and paraffin wax in turpentine.

Zinc soaps find their greatest use in the cosmetic and pharmaceutical industries. Zinc stearate is incorporated in face powders in amounts up to 10 per cent to increase the hiding power and adhesion and to increase the smoothness of the powder. Magnesium stearate is lighter and fluffier and is replacing zinc and aluminium in this application to some extent, as little as 4 per cent giving the same results as 10 per cent of zinc stearate.

The use of zinc soaps and, more commonly, of copper and mercury soaps as anti-fouling paints for boats and marine structures is well known and their efficacy is due to their toxicity to marine organisms.

(j) LUBRICANTS

The theory and practice of lubrication form a highly specialized branch of engineering and numerous excellent text-books are available dealing with the various phases of this important subject. It is outside the scope of this Bulletin to consider this vast field in any great detail, but a few principles may be given, together with some examples in which marine animal oils are used in the compounding of lubricating materials.

When two surfaces are made to slide over each other, the motion is resisted by a force called friction. This friction is due to the interlocking of minute irregularities in the surfaces and also to the adhesion between the parts in close contact. The purpose of lubrication is to reduce this friction and it is accomplished by putting a third substance, the lubricant, between the sliding surfaces. The nature of the lubricant is very important; most lubricants are liquids but not all liquids are lubricants. In industrial machinery practically all moving parts that require lubrication are made of metal and it has been found that mineral and fatty oils are the most efficient lubricants for this purpose. By reason of their cheapness and certain physical and chemical properties, mineral oils have come into general use as lubricants, but there are purposes for which animal fats are still required.

Among the properties that a good lubricant should possess, the following are the most important:

Oiliness may be defined as the power of a lubricant to maintain a film between two surfaces even when under heavy loads; it depends more upon the chemical nature of the lubricant than upon the physical, and appears to be due to the action of the lubricant on the surface. The wetting power of an oil is, in part, a measure of its oiliness. Oiliness is possessed by animal and vegetable oils to a greater extent than by mineral oils.

Chemical stability is of great importance in lubricants, particularly where high temperatures are encountered. Oxidation of mineral and fatty oils causes the formation of gums, and the products of oxidation may be acidic in nature, thus causing damage to the metal parts.

Viscosity in a lubricant should be high enough to maintain an unbroken film between the

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lubricated parts, but it should not be too high since high-viscosity oils have a frictional resistance within themselves. The maintenance of an unbroken film is now recognized as being more a function of the oiliness than of the viscosity.

Uniform consistency at different temperatures is a characteristic much to be desired in a lubricant. Increase of temperature decreases the viscosity, and, in cases where the oiliness of the lubricant is also low, a temperature may be reached at which the continuous film may not be maintained. On the other hand increase of pressure increases the viscosity, and in extreme cases the frictional resistance of the oil may prevent proper lubrication. Both temperature and pressure affect the viscosity of mineral oils to a greater extent than that of fatty oils.

Freedom from corrosive acids. Lubricants should be of neutral reaction or, if slightly acid, should not corrode the metal parts to which they are applied. Oils that oxidize and form gum produce acidic by-products which have a corrosive action. Small amounts of free fatty acids have been shown to be harmless in this respect.

Minimum coefficient of friction is required in lubricating oils. Fatty oils containing small amounts of free fatty acids have a lower coefficient of friction than neutral oils. The coefficients of mineral oils can be reduced by blending with fatty oils or with small amounts of free fatty acids.

There are two types of lubrication. In one, the so-called boundary type, the lubricant exists as a very thin film of oil between the two surfaces. This film is maintained by adsorption of the lubricant on the surface of the metal. In the case of fatty acids the adsorbed layer consists of molecules orientated so that the hydrocarbon portion stands out from the surface. Mineral oils also form films but they are not as stable as those formed by the fatty oils. When the lubricant is present between two surfaces in amount greater than that required merely to give a film, the chemical nature of the lubricant becomes of less importance and physical properties such as viscosity assume greater significance. This is the fluid type of lubrication.

(i) NON-BLENDED OILS, SPINDLE AND LIGHT OILS

Oils of this kind are used in the boundary type of lubrication and the surfaces being lubricated are continuously wet by the film of lubricant. For watches and other fine instruments the head and jaw oil of porpoises and dolphins has been used for years with excellent results. These oils combine the properties of great oiliness, low viscosity and chemical stability and in addition they remain fluid at very low temperatures. These properties are most likely, in part, due to the peculiar composition of these oils, iso-valeric acid (see Section 2) being present in considerable amounts. The scarcity of porpoise jaw oils has led to the development of other lubricants for fine mechanisms, mixtures of neatsfoot oil and mineral oils being used to a great extent. German patent 538,387 describes a synthetic oil made by the esterification of fatty acids having from 5 to 12 carbon atoms in the chain, thus giving in effect a synthetic porpoise jaw oil.

Sperm oil from which the spermaceti wax has been removed finds use as a lubricant for high speed spindles and looms. Sperm oil shows but little tendency to oxidize, has a low viscosity and high "oiliness" characteristics. A fish liver oil that possesses many of these qualities is that obtained from the ratfish (see Section 10). This oil is not very highly unsaturated, having an iodine value of but 85 to 90, but remains clear down to −3°C. (26.6°F.). It contains

considerable unsaponifiable matter, does not gum readily and possesses great oiliness, particularly when a trace of free fatty acids is present.

(ii) BLENDED OILS

Nearly all fatty oils are soluble in all proportions in mineral oils, and mixtures of the two are used in a great variety of lubricants for various specialized purposes. The fatty oil increases the oiliness of the mixture and lowers the coefficient of friction. The increased oiliness is particularly marked in cases where the lubricant is subjected to high temperatures or to moisture. It is therefore common to find such blended oils used in internal combustion engines, steam engines, etc. Raw and blown rapeseed or castor oils are used to a great extent for this purpose, but the use of other oils with similar properties is becoming more general. Such a blown oil must be miscible with mineral oil and give no settling on cooling. The unsaturation is not extremely important, but the oil should be free from odour and should not have more than 6 to 7 per cent free fatty acids. The function of the fatty oil is chiefly to make the mineral oils emulsify with water.

There are numerous patents describing the preparation of fish oils for use in blended lubricants. Japanese patents 99,215 and 101,303 cover the polymerization of a fish oil. In the first patent the oil is hydrogenated to an iodine value of between 120 and 150 and then polymerized in the presence of a catalyst. According to the second patent a fish oil is cold-cleared at 0°C., polymerized at 250° to 300°C. in the absence of air, and then steamed. In both cases the oils are mixed with mineral oil to form a lubricant. A viscous lubricant, of relatively low tendency to form surface films and suitable for dissolving in hydrocarbon oils, is made according to U.S. patent 2,133,493 from the polymerization product of a semi-drying oil such as fish oil admixed with 0.01 to 0.05 per cent of sulphur, selenium or tellurium which serve as stabilizers. U.S. patent 2,107,316 describes how a fish oil may be polymerized by the action of a high-voltage electric discharge, stabilized by hydrogenation and the product used as a lubricant after suitable blending with mineral oil.

The use of polymerized fatty oils in blended mineral oils assists in depressing the "pour point" and several patents covering this usage have been issued. According to British patent 463,932 unsaturated oils are polymerized with a boron halide and the polymer treated with a selective solvent that removes the non-polymerized portion of the reaction mixture. The polymerized ester or oil is blended with mineral oil and it is claimed that the product not only depresses the pour point but facilitates the separation of wax in the de-waxing process. The production of non-freezing lubricating oils has been studied by Tanaka, Kobayasi and Tsukada (1935), who found that a mixed-base mobile lubricating oil with a melting point of −1°C. had its melting point depressed to −15°C. by the addition of 0.08 per cent of hydrogenated sardine oil with a melting point of 56°C. The addition of saturated fatty acids of high molecular weight also has the effect of lowering the melting point of a mineral oil, 0.2 per cent of myristic, palmitic, stearic or behenic acids lowering the melting point of a spindle oil from its original value of −42°C. down to −60°C. These authors also investigated the effect of the addition of polymerized fish oils to lubricating oils and found that a sardine oil polymerized at 300°C. for 3 hours, when added to a mineral oil in the amount of 2 per cent, lowered the melting point of the latter from its original value of −34°C. to a value of −60°C. Greater polymerization of the fish oil or its addition in larger amounts did not have any further effect on the melting point of the mineral oil.

A method for making synthetic lubricating oils is described by Kuwata, Matubara and Asahara (1940) which involves the dechlorination of hydrogenated fish-oil fatty acids previously treated with chlorine gas at 100°C. in the presence of light. The dechlorination process is aided by catalysts such as acid clay, but it was eventually discovered that a better product could be

made by using lime in the dechlorination process. Hydrogenated fish-oil fatty acids of iodine value 4.9 and melting point 48.3°C. are chlorinated until 1.5 to 2 atoms of chlorine per molecule of acid has been absorbed. One hundred parts of these acids is dissolved in 200 parts of petroleum hydrocarbons of boiling point 320° to 350°C. (and which has previously been rendered inert by treatment with aluminium chloride) together with 40 parts of lime and 20 parts of acid clay. The mixture is slowly heated to 330°C. when dechlorination and splitting off of the carboxyl group occurs. The synthetic oils are hydrogenated and then dewaxed at a temperature of −18°C., using as solvent a mixture consisting of 35 per cent acetone and 65 per cent benzene. The synthetic oils so produced are said to meet the requirements of high-grade lubricants.

(iii) LUBRICATING GREASES

These products cover a very wide range of materials made for various specialized purposes. Most of them contain sodium, potassium, calcium, lead or aluminium soaps blended with mineral or fatty oils. They may or may not contain water. Greases are solid lubricants and are used chiefly for gear lubrication. The soap functions as a stiffener, giving body and rigidity to the grease. Horse fat, tallows, palm oil and various other low-priced fats or oils are used for grease soap. Free fatty acids are also used for some greases, stearic and oleic acids chiefly being employed. The soaps are actually made in the grease pan with the hydroxides of the metals mentioned above, mineral oil is blended in and the mixture heated until the required consistency is obtained.

Raw fish oils are used in a few special greases. Lead fish-oil soaps are used in the manufacture of some hypoid gear lubricants, about 22 per cent of the finished lubricant being soap. U.S. patent 932,855 describes the preparation of journal oils that are made with tallow and lead fish-oil soaps, 750 pounds of fish oil and 600 pounds of lead oxide being used for blending with 7 tons of tallow. U.S. patent 2,133,493 covers the use of sulphurized fish oils in lubricants for hypoid gears, 20 per cent of the sulphurized oil being blended into black mineral oil. Fish oils treated with sulphur chloride have also been recommended as bases for extreme-pressure lubriants. Klemgard (1937) states that "large quantities of these products (fish oils) are consumed in compounding car oils and various special machinery oils. . . .".

The use of processed fish oils in compounding greases seems to be entirely an economic matter. It is possible to make solid and semi-solid fats or fatty acids by the hydrogenation of certain fish oils that are entirely suitable for grease manufacture. For instance, a fish oil hydrogenated to an iodine value of 3 or 4 can be utilized for the production of free fatty acids that satisfactorily replace commercial stearic acid. Such fatty acids should have a titre of about 53°C., should consist of at least 98 per cent of free fatty acids, and should have a saponification value of about 200. Red oil or commercial oleic acid that is much used in certain grease formulas can be replaced by fatty acids made from a partially hydrogenated fish oil. Such acids should have an iodine value of 50 to 55, a saponification value of at least 195 and should contain at least 98 per cent free fatty acids. The maximum unsaponifiable matter allowable is 1 per cent. Sheely (1936) has pointed out the advantages of fatty acids over neutral oils in grease manufacture, and it appears definite that the use of such free fatty acids is increasing in the grease-making industry. A larger use of fish-oil fatty acids for this purpose will be governed largely by the relative cost of these materials.

(iv) CUTTING OILS

These are used for two general purposes, namely, as lubricants and as cooling media. In addition, cutting oils remove the accumulated chips in front of the cutting tool and act as a rust preventative. Although there is a large number of cutting oils in use, they may be divided into two general types, the so-called soluble or emulsifying oils and the straight non-emulsifying oils. According to Huffman, Harding and Oldacre (1934) the fundamental characteristics governing the selection of these two types of lubricants are as follows: *soluble cutting oils*, (1) ability to emulsify, (2) tendency to remain stable without separation, and (3) tendency to prevent corrosion and give satisfactory finish; *non-emulsifying cutting oils*, (1) quantity and nature of saponifiable matter present, and (2) quantity of combined sulphur.

In the manufacture of soluble cutting oils, mineral oils are mixed with fatty oils, fatty acids, alkali and water. Rosin acids are sometimes used in the place of fatty acids. Water is usually added before immediate use, the quantity added depending upon the nature of the emulsion required. Emulsifying agents other than alkali soaps are sometimes used; these usually consist of sulphonated fish oils. In a typical formula 9 gallons of mineral oil, 3 gallons of rosin oil and 1 gallon of oleic acid are mixed with 4 ounces of sodium hydroxide dissolved in 1 quart of water and a quart of alcohol. Water is then added to the mixture as required. Practically all emulsifying oils contain the sodium, potassium or ammonium soaps of oleic acid and for this purpose the fatty acids from partially hydrogenated fish oil should prove adequate. The main consideration is that the alkali soap should not tend to precipitate out and should give a good emulsion with the mineral oil.

Non-emulsifying cutting oils are usually mixtures of lard oil and mineral oils with or without free or combined sulphur. The sulphur is commonly combined with the lard oil or other fatty oil and the sulphurized product dissolved in the mineral oil. A heavy-duty cutting oil is made as follows: 26 parts by weight of herring oil is mixed with 10 parts of sulphur and heated to 150°C. (about 300°F.) until all the sulphur is combined. A soft rubbery mass is produced, which is then dissolved in 80 parts of mineral oil by heating to about 65°C. (150°F.). Other unsaturated fish oils may be used in place of herring oil and the writer has found pilchard stearine (iodine value about 120) to be suitable for this purpose. Such sulphurized fish oils are dissolved in mineral oils usually in amounts up to 10 per cent. This type of lubricant is suitable for iron and steel cutting but may not be used on brass owing to the action of the sulphur on the copper.

Thread-cutting oils are sometimes made from certain fish oils. A typical oil for this purpose is made by mixing 20 parts by weight of whale oil with 5 parts of tallow oil and 75 parts of mineral oil. In such mixtures the oiliness factor is of extreme importance and the use of fatty oils is practically essential. Other fish oils may be used in place of whale oil, particularly those of medium unsaturation. Any tendency towards rancidity may be prevented by the use of suitable antioxidants.

(*k*) TIN-PLATE

In making tin-plate, clean sheets of steel are dipped in a bath of molten tin, passing through a layer of zinc chloride flux that covers a part of the tin surface. The sheets are carried out of the bath by rolls and pass through a layer of oil that covers the exit portion of the tin bath to a depth of about 15 inches. The purpose of this layer of oil is to prevent oxidation of the tin and to dissolve any tin oxide that may be formed. The temperature of the tin is kept at about 315°C. (600°F.) and that of the layer of oil at about 240° to 250°C. (464° to

482°F.). Up to the present time palm oil has been used almost exclusively for this purpose. With this oil care has to be taken that the temperature does not become too high, as polymerization is apt to take place and the oil loses its power to keep the plates clean and is also carried off on the plates in excessive amounts. Collins and Clarke (1920), in an effort to find some fat that would successfully replace palm oil, investigated the use of hydrogenated cottonseed oil and hydrogenated herring oil. The former material was used in a plant for a considerable time (12 weeks) and the operation was somewhat better than with palm oil. The iodine value of the hardened oil was 13. A herring oil hydrogenated to an iodine value of 60 was investigated by laboratory methods, and it was found that the product showed less tendency to polymerize or lose weight when heated than either palm oil or the hydrogenated cottonseed oil. These authors concluded that a herring oil hydrogenated to a lower iodine value than 60 would probably prove superior to hardened cottonseed oil for use in tin pots.

According to one manufacturer a good oil for tin-plating should be free from moisture, should contain only a trace of ash, not more than 5 per cent free fatty acids and should not froth when heated to a temperature of 290°C. (554°F.). In addition such an oil should not show a greater increase in viscosity when held for 7 days at 260°C. (500°F.) than is shown by palm oil held under the same conditions.

Theoretically, hydrogenated fish oils should be suitable for this purpose. The greater average molecular weight of the component fatty acids of these oils gives the hydrogenated product greater stability at high temperatures. Thus hydrogenated fish oils have higher smoking points than similarly hydrogenated vegetable oils; their loss on heating is lower and, if properly hydrogenated so that all polyethylenic acids are reduced, they show less tendency to polymerize at high temperatures.

The consensus of opinion among practical tin-plate manufacturers is that no economic substitute has yet been found for palm oil. Some firms have used hydrogenated cottonseed oil successfully and will continue to do so, so long as the product is cheaper than palm oil. All manufacturers agree that, technically, hydrogenated fats can replace palm oil, but in order to do so economically there must be some price advantage. The use of hydrogenated fish oils in the tin-plate industry therefore depends upon the economic aspects of the hydrogenation process.

(*l*) INSECTICIDES

The use of fish oils in insecticides has developed practically entirely as a result of efforts to control the ravages of the codling moth in apple and pear orchards. The oils may be used in three distinct ways. In the first, the oil is used as such, dissolved in kerosene, as an adhesive for arsenical and fluoride insecticides. In the second, the oils are used as fish-oil soaps, water solutions of which appear to have some merit as spreaders for inverted spray emulsions. A third manner of fish-oil utilization in this field is in the preparation of tree-banding compounds in which the fish oil acts as a sticky adhesive, preventing the infestation of the tree by larvae from the ground.

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Webster, Marshall, Miller and Hansberry (1932) have described the experimental work that led up to the utilization of fish oils in sprays used for the control of the codling moth in the north central Washington fruit district. Early experiments had demonstrated that the addition of fish oil to a lead arsenate resulted not only in a better type of coverage on the fruit, but also in an increased deposit of lead arsenate. Analysis showed that there was but little difference in the amount of lead arsenate deposited at the time of actual spraying, but in sprays containing as little as ¼ per cent of fish oil there was an increased tenacity of the deposit that enabled it to weather better. Of the fish oils available it has been ascertained that herring and dogfish liver oils are most suitable. The faster drying oils such as menhaden, sardine or pilchard oils form a hard varnish-like film over the fruit and the insecticide particles are not so easily picked up by the larvae. In general, a slow-drying oil is required that will remain liquid down to 40°F., although in the later types of inverted sprays the liquid nature of the oil is not so important. Salmon oils have been investigated but have proven to be too variable in nature to be used consistently.

Marshall (1937) describes experiments on the development of inverted-spray mixtures for the control of the codling moth. An inverted-spray mixture is one in which a suspended solid, initially wetted by water, becomes wetted by oil prior to or at the moment of impact on a sprayed surface. These inverted-spray mixtures cause a remarkable increase in solid deposit. This characteristic depends upon the solid particles being coated by a film of oil, yet not loosely dispersed in it. Actual experiments showed that these oily deposits, such as those of arsenic, were more effective in preventing the establishment of codling-moth larvae than non-oily deposits of similar composition and amount. The greatest advantage of the oily deposits from inverted-spray mixtures is, however, in their weathering characteristics, virtually no loss being found during dry atmospheric conditions. According to Marshall and Groves (1938) an inverted-spray mixture containing herring oil is prepared as follows: Solution A. 19 parts of a solution of herring oil in kerosene (1:3) is mixed with 1 part of high-grade oleic acid. Solution B. 1 part of monoethanolamine or 1 part of 28 per cent ammonia is dissolved in 12 parts of water. Half-a-pint of solution B is stirred into 1 gallon of water followed by half-a-pint of solution A and the mixture thoroughly beaten up. The resulting emulsion is then added to 100 gallons of water containing 3 pounds of lead arsenate and the whole thoroughly mixed. For heavy spraying, 75 gallons of the above mixture is required per tree.

This method of codling-moth control is now a standard practice in the state of Washington. For some time a herring oil with an iodine value ranging from 135 to 138 was used, but more recently a hydrogenated herring oil with an iodine value of about 90 and a titre point of 35 has been found to be equally satisfactory.

In British Columbia orchards the use of this inverted-spray mixture has not been introduced, chiefly because of the lack of suitable washing apparatus for removing the arsenic deposit from the mature fruit. The Department of Agriculture is experimenting with bentonite-nicotine-sulphate mixtures, using herring oil as an adhesive, for the control of the codling moth in British Columbia orchards. In other parts of Canada fish oils are used to limited extents in the fruit industry. In Ontario, though it is seldom necessary to spray for the control of the grape berry moth, when spraying is resorted to, a quarter of a pound of fish oil is used per 40 gallons of spray mixture. Cod oil has been used in this province for the control of red spiders on raspberries, but, although

proving to be efficient at low concentrations, the oil caused some leaf injury. It is the opinion of agricultural officials that, if fish oil soaps were readily available, small quantities could be utilized as a supplement for nicotine sprays, as these soaps have been found to be an excellent spreader for such sprays. Canadian Industries Ltd. (private communication) have made some experiments with a saponified herring oil and found it to have excellent spreading properties for nicotine and in addition to have a unique flocculating effect on suspended insecticidal materials such as lead arsenate and cryolite.

The use of fish oils in pomological sprays is mentioned in many reports. Haller, Cassil and Murray (1938) state that the addition of fish-oil or mineral-oil emulsion to the first two lead arsenite sprays and fish oil to late-cover sprays of casein lime does not greatly influence the removal of the lead residue at harvest time. Black (1936) claims that apple and pear trees sprayed about four weeks before blossoming with a raw linseed-oil or seal-oil emulsion produced an earlier, more prolific and more even bloom, by which the crop was considerably enhanced in value. Zappe and Stoddard (1937) report that sprays made with 3 pounds of lead arsenate, 10 pounds of hydrated lime and 100 gallons of water with an adhesive of fish oil gave excellent control of curculio, codling moth and other chewing insects in Connecticut orchards. Hood (1929) claims that the use of fish oil as an adhesive in lead arsenated sprays for gypsy-moth extermination and general control work permits the reduction in quantity of lead required. Fish oil is also a good adhesive for Bordeaux mixture. Miller (1937) found that foliage injury resulting from the treatment of walnut trees was almost completely eliminated by the addition of emulsions of salmon oil or of certain kinds of mineral oil to the spray. U.S. patent 2,127,380 describes the preparation of an insecticide by reacting a solution of an alkali metal arsenite with an inorganic cupric salt and an alkali metal salt of fatty acids from vegetable, animal or fish oils. The resulting complex product can be used as sprays for foliage. Canadian patent 284,093 deals with the production of a paper for use in tree-banding. The paper is covered with a composition consisting of 1 part of rubber latex, $\frac{1}{2}$ a part of fish oil, 15 parts of mineral oil, $\frac{1}{2}$ a part of rosin and 1 part of molasses or other sweetening material. The reaction product of thiodiphenylamine with an unsaturated fatty oil such as soybean or fish oil is protected by U.S. patent 2,127,039 for use as a 5 per cent solution in mineral oil in horticultural sprays.

(m) LEATHER

Over 8,000 tons of raw, refined and sulphated (including sulphonated) marine animal oils are used annually in the leather industries on this continent. A survey carried out early in 1939 from this Station indicated that over 600 tons of such oils are used in the Canadian leather industries. Much of this Canadian consumption is supplied either directly or indirectly from the Maritime provinces, which within recent years have produced an average of about 500 tons of cod oil annually. Besides cod oil, other marine oils used in Canadian leather industries include whale, seal, salmon, herring, pilchard, menhaden, shark and dogfish oils. Some of these are imported, particularly in sulphated form, and some Canadian oils are exported for leather trades elsewhere. With the advent of war in 1939, there has been a tendency toward a decrease in availability of Canadian cod oil with the result that other Canadian marine oils are being viewed with renewed interest as supplements.

Animal and vegetable oils, fats and greases, together with mineral oils and greases, are all used in the leather industries, and marine animal oils participate

very greatly in this consumption as they are particularly suitable for one purpose or another in almost every process for the finishing of leather. The following paragraphs briefly indicate these uses and processes with particular reference to the applicability of marine animal oils. The subject of patent and enamelled leathers is treated under I(e) of this Section.

Oils, fats and greases when used in the preparation of leather as the "tanning" agent in the process known as "oil tannage" have functions different from what they have when used as an adjunct before, during or after the tanning of leather by actual tanning agents. When used alone in the process known as oil tannage, fat tannage or chamoising, e.g. preparation of wash leather and washable gloving from the "splits" of sheep or goat skins, the oils react with the proteins of the skin, thereby making them non-putrescible through processes akin to tannage. At the same time, some of the oil produces in the material the desirable physical properties of increased softness and resistance to cracking and moisture penetration. When used as adjuncts to other tanning processes, oils serve the following purposes: (1) They may be added during the tanning process to prevent too much tanning material from being taken up by the leather, and to prevent excess friction during the mechanical process of drum tanning; under other conditions they may be necessary to increase the absorption and penetration of the tan liquors. (2) They increase the softness, tensile strength, flexibility, and resistance to cracking and moisture penetration; these effects are chiefly due to their physical action of penetrating and lubricating the main fibres of the grain and maintaining the smaller individual fibrils in the separated state induced by a previous (sometimes subsequent) treatment of the leather with water. (3) They assist in securing the desirable light colour of the leather surface by hindering the migration of excess of tanning agents to the finished surfaces during drying; this effect is produced only if the oil penetrates the leather—oils applied to the surface of dry leather darken it.

The processes in which marine animal oils may be utilized to secure these effects are described briefly in the following paragraphs.

(i) OIL OR FAT TANNAGE

This is used for preparing chamois, buff, Japanese white, Napa, buckskin, mocha, fur skins, deer skins, and other soft leathers. The moist "splits" are impregnated with a drying oil by swabbing or mechanical beating. This treatment is interrupted from time to time by hanging up the skins to cool and to take up the oil through evaporation of some of the moisture. The skins are finally either hung up in warm (100°F.) rooms, piled loosely, or stored in an enclosed space. Oxidation of the oil occurs, and some of the oxidation products combine chemically with the collagen and other nitrogenous constituents of the skin to produce the desired "tanning" effect. If piled or stored, heat is generated spontaneously and the temperature has to be kept below about 130°F. The skins are then soaked in warm water and by hydraulic pressing, a certain excess of free fat or grease known as "moellon" or "dégras" is recovered. They may also be scoured with alkaline solutions and pressed to remove remaining excess of free fatty material which, when recovered from the alkali by acidification, is known as "sod oil". Final drying, working, bleaching and buffing of the skins yields a finished product that is very soft and open.

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The oils used in fat tannage are almost invariably marine animal oils; cod, herring, menhaden, pilchard, sardine, salmon, whale, seal, dogfish and some other shark oils are commonly employed. Mineral oils have no "tanning" powers. Meunier (1918) concluded that the superiority of fish oils was due to the presence of characteristic fatty acids containing four unsaturated bonds. Later work has confirmed this conclusion, and indicated that the failure of linseed oil to compete with fish oils is due to the following considerations (Dean 1938): The average total percentage of unsaturated constituent fatty acids in the glycerides of linseed oil is greater than the average for cod-oil glycerides, but linseed-oil glycerides contain little, if any, of the types of fatty acids found in cod oil which possess the four (or more) unsaturated bonds considered necessary for tannage. Moreover, assuming even distribution of fatty acids among the glycerides of each oil, most of the cod-oil glycerides will contain at least one "inactive" (not easily oxidized) saturated or mono-unsaturated fatty acid, while not more than about half the glycerides of linseed oil will do so. Hence each cod-oil glyceride that combines chemically with the leather, and escapes later removal by degreasing operations, probably contains an inactive fatty group which is capable of lubricating the leather fibres; with linseed oil, however, there is less total chemical combination with the leather and, of those glycerides that escape removal, only about one-half will contain lubricating groups. Unsaturated free fatty acids in these commercial oils may exert some tanning action if sufficiently unsaturated; the remaining acids are most likely to be removed during degreasing. The foregoing offers a possible explanation of the "harsher" tannage resulting from free fatty acids and too highly unsaturated oils.

(ii) STUFFING OF TANNED HIDES

Leather produced by tanning procedures other than oil tannage also requires the application of oils at some stages of the process. Although a slight degree of oil "tanning" may result from chemical action of the oils, this is a subsidiary effect; the main purpose in the application of the oils is to secure the earlier-mentioned desired physical properties imparted to the leather by oils.

"*Oiling-off*" involves the swabbing of liquid oil over the grain surface of moist leather. As the moisture later evaporates the oil is drawn into the leather, thereby lubricating the grain; the tan liquor is hindered from collecting and evaporating at the surface to cause crackiness and darkening of colour. Since no chemical oxidation of the oil is required almost any animal or vegetable oil without pronounced drying qualities may be employed. The oils chiefly used, however, are cod oil, sulphated cod oil, and mineral oil emulsified with sulphated cod oil. Whale, seal, salmon, dogfish and shark oils should also be suitable. Mineral oils alone are not entirely satisfactory; they are not absorbed or "fixed" by the leather to the same degree as are fats and fatty oils, which possess the peculiar attribute of "oiliness" (Section 9 I (f)).

"*Hand stuffing*" involves the rubbing of an oily paste ("dubbin") into the flesh and grain surfaces of moist leather when a finished product containing up to 15 per cent fatty material is required. The oil is used in paste form to allow it to be held against the leather during the period of hanging while the water evaporates from the leather. The oily constituent preferred is usually cod oil, although herring, sardine, pilchard, menhaden, salmon, and some shark and whale oils are used. A moderately high unsaponifiable content in the oil is desirable for heavy leathers. The solid constituent of the paste is often an animal tallow or other hard fat or wax, although

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the binding function of a powder such as French chalk has been used. Hydrogenated marine animal oils are also suitable as a binder. The oily constituent penetrates the leather, while the solid constituent either remains on the surface to be scraped off and possibly used over again, or at most remains in the surface layer. The paste must therefore be separable into its two constituents and a truly homogeneous paste of oil plus a mineral jelly or grease will not function satisfactorily.

Drum stuffing involves much the same principles as the two foregoing operations except that the mechanical agitation and beating employed at an elevated temperature (from 120°F. for vegetable-tanned leather up to 212°F. for chrome-tanned leather) allows the incorporation of not only oils, but also greases, solid fats and waxes into the moist leather in greater quantities and in less time than by the foregoing two processes. Up to 25 per cent fatty material may thus be incorporated. The amount of moisture in the leather during drumming must be carefully controlled in relation to the fat used and the physical properties desired in the finished product. A wide variety of materials may be used, among which the following marine animal oils have found favour: cod, menhaden, whale and salmon. The dégras and sod oil by-products of oil tannage are also used. These may be supplemented by similar products artificially prepared by partially "blowing" fish and whale oils. For the stuffing of sole leather, a Canadian manufacturer has expressed the following order of decreasing preference: cod, pilchard, whale, salmon, herring, seal, shark, dogfish, sardine, sperm. Free fatty acids up to 9 per cent (as oleic) are not objectionable, and the presence of cholesterol (as in fish liver oils) was stated to be desirable. Hydrogenated, sulphated, and "blown" fish, whale and seal oils as well as commercial "oleic" and "stearic" acids are also used.

Burning-in involves the hand application of molten fatty materials to absolutely dry leather at temperatures of about 190°F. The fat is rapidly absorbed by the leather, which is then hung up to cool. *Dipping* is a similar process, whereby the leather is dipped into a vat of the molten fatty material; there is not as close a control over the amount of fat absorbed as in the burning-in method. Following the application of either of these methods, the dry, impregnated leather is usually drummed with warm water. The final product will thus have undergone the same treatments as in the drum-stuffing method except that these have been applied in the reverse order. An advantage of burning-in and dipping methods is the practicability of incorporating high-melting fats or waxes into leathers where a high degree of waterproofing is desired.

Fat liquoring involves the treatment of moist hides or tanned leather with fats or mineral oils in emulsified form. The operation is carried out with the liquor at an elevated temperature, *e.g.* 120° to 140°F.

For hides, the process consists of a simultaneous tanning and oiling, the presence of the emulsified oil serving to prevent too much tan liquor being taken up during tanning and to reduce the friction of the hides against one another and the revolving drum. A typical drum charge for such a purpose may contain 1,600 parts of aqueous tan liquor, 40 parts of mineral or other non-drying oil, and one part of sulphated fish oil as emulsifying agent.

In the case of fat liquoring of tanned leather, the object is to incorporate a moderate amount (up to 10 per cent) of fatty material throughout the whole body of the leather in a uniform manner and in a reasonably short time, *e.g.* 30 minutes. The emulsification of the oil with water allows rapid interchange of water and oil between the fibres without its being necessary to force the fatty material into the moist leather as in drum stuffing, or to await the evaporation of the moisture for the purpose of drawing in the oil as in oiling-off and hand stuffing. Fat liquoring may be employed before or after dyeing, and involves many other considerations for which the literature of leather tanning and finishing must be consulted.

Many types of non-drying animal, vegetable or mineral oils are used for fat liquoring, alone or in combination. Of the marine animal oils employed, cod oil is the most popular. Other non-drying marine oils including salmon, dogfish, shark, whale and seal oils and the dégras and sod oil resulting from cod-oil tannage are also in demand. Salmon oil is a close competitor of cod oil.

As emulsifying agent, soap, egg-yolk, dégras, sulphated or sulphonated oils and fatty alcohols are used. Egg-yolk causes practically no "fixing" of the oil in the leather, i.e. it may be extracted almost entirely by fat solvents; soap allows small amounts of oil to be fixed, whereas, when sulphated or sulphonated oils are used, appreciable amounts of oil are fixed in the leather (Theis and Graham 1934). Hence sulphated and sulphonated oils in a fat liquor serve as more than mere emulsifying agents and their introduction opened up a new field of approach in fat liquoring. Blancher (1938) has indicated the advantages of the newer fatty alcohol derivatives. It is of interest to note that the use of sulphated oils for the impregnation of leather intended for gas masks confers upon the leather a considerable impermeability toward mustard gas (Nicolae 1935). Soaps and alkaline emulsifying agents have a disadvantageous tendency to remove vegetable tannins and dyes during fat liquoring; moreover, soap emulsions may be broken by acid leathers or tanning salts. Sulphated or sulphonated emulsifiers overcome these difficulties. Practically any marine animal oil except the most highly unsaturated body oils (e.g. pilchard) provide suitable sulphated emulsifying agents. In the 1939 survey referred to previously, various Canadian leather firms pronounced sulphated cod, salmon, herring, whale, seal, sperm, and even pilchard oils satisfactory in the order given; the original oil should have an iodine value not much over 150, the stearine content should be as low as possible; opinion was divided regarding unsaponifiable content.

Some unpublished experiments carried out by Brocklesby and Rogers in these laboratories in 1939 were designed to assess the relative sulphating properties of British Columbia pilchard (heavy pressed), herring, salmon, whale, sperm, halibut head and dogfish liver oils as compared with those of two commercial samples of Canadian east coast cod oil. Both "high" and "quick" sulphation processes (Section 8 II (e)) were employed.

For high sulphation, 27 parts by weight of concentrated sulphuric acid were slowly (1.5 to 3 hours) added, with mechanical stirring, to 100 parts of oil at a temperature not exceeding 35°C. (95°F.). The stirring was continued for a further 6 hours, and the product poured into twice its volume of a 10° Baumé solution of sodium sulphate heated to 40°C. (104°F.). After this was agitated and allowed to stand overnight, the sulphated product that separated was made almost neutral to methyl orange by the addition of caustic soda solution; almost boiling water was added, and the mixture was shaken and again allowed to separate (2 to 12 hours). The sulphated layer was finally treated with sufficient concentrated caustic soda solution to render it clear on shaking.

For quick sulphation, 22.5 parts of concentrated sulphuric acid were added with violent agitation to 100 parts of oil within 10 to 12 minutes, keeping the temperature below 54°C.(129°F.). Stirring was continued for 50 minutes longer, and the product poured into twice its volume of cold, 10° Baumé caustic soda solution. After this was agitated and allowed to separate for about one hour, the remaining operations were conducted as described in the preceding process.

Pilchard oil. Difficulty was experienced in maintaining the temperature below 54°C. during quick sulphation and there was evidence of polymerization and condensation. The product from both processes tended to set solid and become cloudy, but was reversibly liquefied and cleared by warming. Raw and heavily-bodied pilchard oils gave almost the same results as the heavy pressed oil.

Herring oil (high sulphation only). The acid had to be added very slowly to maintain the temperature below 35°C. The final product was at first clear, but, on standing, became opaque and quite viscous, though not to the same extent as the pilchard oil products.

Salmon oil. The high-sulphated product could not be cleared with the caustic soda wash, but the quick-sulphated product was the best of all those prepared in the experiments; it was slightly reddish and remained clear for a long time, although eventually a slight suspended cloudiness appeared.

Whale oil (high sulphation only). The product was at first clear but almost immediately deposited a small amount of dense white material, some of which remained suspended to impart an opaqueness to the liquid.

Sperm oil. The clear, light-coloured product from high sulphation separated a thick white material on cooling which was reversibly soluble on warming. With quick sulphation, no satisfactory product could be obtained due to poor separations and refusal to clear with caustic soda.

Halibut head oil. High sulphation was unsatisfactory; the final product was at first clear, but some 10 per cent of a murky aqueous layer separated on standing, and the oil became opaque, and finally set to a semi-solid viscous mixture. The clear, quick-sulphated product became slightly cloudy and viscous on standing, but not to the same extent as the high-sulphated product.

Cod oil (high sulphation only). The process proceeded normally to yield a final product quite dark in colour. One sample on long standing deposited a considerable amount of solid white material.

Table LXII presents some data pertaining to these products, and summarizes observations made on diluting them with water.

TABLE LXII. Data and observations on sulphated fish oils

Sulphated product	Water in original product (%)	Sample diluted to contain 50 per cent of water			Behaviour on diluting with 10 volumes of water
		Free alkali as KOH (%)	SO₃ (%)	Appearance	
Dogfish liver oil, quick-sulphated	41.0	0.0	2.88	Colloidal emulsion	Very opalescent, clearing on addition of alkali; slight ppt. formed at 50°C.
Dogfish liver oil, high-sulphated	45.0	0.1	1.96	Very thick emulsion	Opalescent, partly cleared by addition of alkali; clear liquid with slight flocculent ppt. at 50°C.
Pilchard oil, high-sulphated	40.5	1.6	1.12	Almost solid with granular precipitate	. . . .
Salmon oil, quick-sulphated	49.0	1.6	5.86	Very slightly cloudy	Extremely murky; cleared by alkali and remained clear at 50°C.
Herring-oil, high-sulphated	18.5	2.3	0.65	Thick, with unsettled gelatinous particles	Murky with white solid ppt. somewhat cleared by alkali; became very cloudy on warming to 50°C.
Cod oil, sample "A", high-sulphated	40.0	0.8	1.96	Slightly cloudy	Slight opalescence cleared by caustic soda; remained clear at 50°C.
Cod oil, sample "B", high-sulphated	40.5	0.2	2.09	Quite clear	As above

Samples of most of the products were tested for their emulsifying properties by thoroughly mixing 40 parts of sulphated oil (containing 50 per cent of water) with 23 parts of mineral oil.

and 37 parts of olive oil. Table LXIII presents a summary of the appearance of the emulsions after they had stood for 5 and 24 hours. After further dilution with 50 per cent more water, shaking and allowing to stand overnight, a marked separation was observed in all samples except that of the quick-sulphated dogfish liver oil, which maintained a stable emulsion for several days. It is stated that the emulsions used in fat liquoring must have sufficient stability not to "break" in bulk form, but that the emulsion should break fairly readily within the leather.

TABLE LXIII. Behaviour of aqueous emulsions of mineral and olive oils with sulphated fish oils as emulsifying agent

Emulsifying agent	Appearance after standing for 5 hours	Appearance after standing for 24 hours
Dogfish liver oil, quick-sulphated	Homogeneous clear solution	Homogeneous clear solution
Dogfish liver oil, high-sulphated	Considerable separation	Marked separation; sulphated phase constituting 41%
Pilchard oil, high-sulphated	Slight separation	Marked separation; sulphated phase constituting 35%
Salmon oil, quick-sulphated	Considerable separation	Marked separation; sulphated phase constituting 46%
Herring oil, high-sulphated	No separation of emulsion	15% clear sulphated phase; 5% supernatant oil; remainder stable emulsion
Cod oil, sample "A", high-sulphated	Slight separation	Marked separation; sulphated phase constituting 35%
Cod oil, sample "B", high-sulphated	As above	As above

In conclusion, it should be pointed out that an important consideration in the use of marine animal oils in any processing of leather is the possibility of "spueing". This is a term used to describe the formation of a film of greasy material on the surface of leather that has been standing for some time. A sticky resinous exudation appears to be due to oxidation products favoured by exposure of the leather to oxidizing conditions such as heat, sunlight and presence of oxidation catalysts (e.g. iron, chromium and copper salts). Stather and Lauffmann (1932) studied such spueing and recommended the avoidance of highly unsaturated fish oils in the processing of leathers tanned with iron salts. A superior protective action of fish oils in the treatment of pulley-belt leathers subjected to uptake of iron compounds from iron pulleys has, however, been claimed (Kubelka *et al.* 1937). Another type of spueing, the formation of a greasy "bloom" on the surface, is due to slow hydrolysis of incorporated oils, with consequent liberation of free fatty acids having a higher melting point than the original fat. Acids with high melting points are not predominant in marine animal oils other than hydrogenated oils. The admixture of mineral oils with fish oils lessens a tendency toward spueing, as evidenced by a typical formula for a fat-liquoring oil: "Cod oil", 20 parts; sulphated-cod-oil emulsifier, 15 parts; mineral oil, 25 parts. A preference frequently expressed for fish oils with a moderate content of unsaponifiable material is also associated with the natural occurrence of spueing inhibitors such as lecithin (and possibly cholesterol) occurring naturally in fish (liver) oils.

There are certain minor industrial uses of fish oils that deserve mention. In addition, processed materials derived from fish oils may have a variety of industrial applications and it is therefore convenient to consider these miscellaneous applications according to materials rather than to the industries using them. Most of the usages to be mentioned have actually been established in industrial practice. In a few cases the usages are taken from suggestions in the literature or from work done in these laboratories.

(a) FISH OILS, MISCELLANEOUS

(i) QUENCHING OF STEEL

This is in some cases carried out by immersing the heated metal in a bath of oil. Whale oil was originally used for this purpose but recent developments in this field indicate that mixtures of oils can be made that are superior in their quenching properties to any single oil. Mineral oils also can be used for quenching high-speed tools. Some of the cheaper semi- or non-drying vegetable oils are more or less satisfactory for any type of steel quenching. However, blends of mineral oil with fatty oils are cheaper and of greater general utility. The fatty oil is used to an extent of about 25 per cent of the mixture and is preferably one that will not turn rancid or form gum when heated. Partially hydrogenated fish oils are satisfactory for this purpose.

(ii) JUTE BATCHING

This and the softening of similar fibres before carding and spinning used to be carried out by treating the raw fibres with oil and water. Whale oil and fish oils were employed for this purpose. Nowadays the fibres are treated with an emulsion of oil and water. Such an emulsion permits more uniform lubrication of the fibres. Mineral oils have to a large extent replaced the use of fatty oils for this purpose largely because of the price and because they do not turn rancid. The function of the oil is to lubricate and soften the fibres, and to accomplish this it is essential that the oil particles adhere tenaciously to the fibres. It is well known that fatty oils are adsorbed on surfaces to a greater degree than mineral oils, and their use in the batching of fibres would be permissible if they were stable to rancidification. Some of the fish liver oils of relatively low unsaturation are quite easily stabilized by partial hydrogenation or by antioxidants and undoubtedly could be used in the batching process.

(iii) OILED FISHING GEAR

Oiled cords and threads, as used in fishing tackle and the like, are usually made with a raw linseed oil, applied without any driers, but dried in cabinets, thoroughly aired and heated to 100° to 150°C. Heavy-pressed pilchard oil can be utilized to advantage in this case as the elasticity and extensibility of the oil

film prevents cracking. The steam-distilled polymerized product from pilchard oil, when dissolved in a suitable solvent such as dipentene, is also of value for oiled cords, it having the added advantage of producing a waterproof film that is still resistant to cracking. In the treatment of textile fishing nets cuprous oxide has found extensive use. This material usually is incorporated in a homogeneous mixture, of which tar is a common constituent. Experiments with the use of certain amounts of fish oils showed that they helped to form a mixture that could be easily applied, but there was some evidence that they diminished the strength of the twine. Inasmuch as linseed oil has been used quite successfully in oiling fishing nets, it is not likely that fish oils would cause any more deterioration than the former oil, since in the drying process, during which oxidation takes place, the formation of organic acids is not greater in drying fish oils than in linseed oil.

In Europe, tanned cotton fishing nets have been treated with shark liver oils containing large amounts of unsaponifiable matter (chiefly squalene). The results are stated to be similar to those in which linseed oil is used.

(iv) RUST PREVENTION

Drying and semi-drying fish oils have been used successfully to prevent the rusting of iron pipes and girders stored outdoors. In some cases the oils are applied directly, after the incorporation of a little drier, but usually they are made up into a black paint with an asphalt base.

(v) MULCH PAPERS

These have been made successfully by impregnating paper with fish oil (Harrison 1931). These papers are used as artificial soil coverings for vegetable and small-fruit gardens and according to a number of authors bring about early, quick-maturing crops. The main function is to prevent weed growth, conserve moisture and heat, and in some cases actually to supply nutrient material. The papers usually contain a black pigment and may also be impregnated with fertilizing and insecticidal materials. Asphalt papers are used to a great extent, but those impregnated with drying or semi-drying fatty oils are capable of longer exposure to moisture on wet soil without becoming defibred or pulped.

(b) FISH-OIL STEARINE

This material is produced from the raw fish oil by cooling and filtering and represents the solid, more saturated portion of the oil. It is usually produced as a soft fat containing appreciable quantities of absorbed liquid oil.

The hardness and unsaturation depend upon the temperature at which the fish oil is cold-cleared and upon the thoroughness with which the stearine is pressed. In its raw state fish-oil stearine has limited applications. Owing to its unsaturation it can be sulphurized, the product being of value in the production of sulphur-base cutting oils. Saponified fish-oil stearine can be used in sheep dips, as suggested by Australian patent 15,258, distilled yacca gum being the active ingredient. Sulphurized fish-oil stearines have also been utilized as insecticides.

Fish-oil stearines can, of course, be used as raw material for hydrogenation for the production of hard fats or saturated fatty acids. A hydrogenated product conveniently made from stearine is utilized in the manufacture of laminated paper which is oil- and moisture-proof and which, according to U.S. patent 2,082,278, consists of 86 parts of emulsified hydrogenated fish oil and 14 parts of a rubber product.

(c) SOLID SATURATED FATTY ACIDS

These acids are made by the total hydrogenation of fish-oil stearine or the whole oil. The resulting solid fat is saponified and the fatty acid recovered by acidification with a mineral oil, as described in Section 8 of this Bulletin. The solid acids have a variety of uses, some of which are dependent upon the degree of unsaturation and/or the titre point.

(i) CANDLES

The chief constituents of candles are the paraffin waxes and beeswax to which are added certain other materials designed to improve the hardness and dripping property of the candles. Of these latter materials saturated fatty acids or hydrogenated fats have proven to be of outstanding value.

So-called "stearic" acid has been a standard commodity as a hardener in the candle industry for many years. It is now realized that the fully saturated fatty acids from fish oils or certain other animal oils as well as the fully hydrogenated fat itself can be utilized in place of stearic acid. In Canada the consumption of stearic acid for candle manufacture approximates 75,000 pounds per year. Several manufacturers have used hydrogenated fish-oil fatty acids with success, but up to the present the supply has been limited and of foreign origin.

The chief criteria by which a stearic acid substitute is judged in candle manufacture are the melting point and freedom from fishy odour when burning. The latter is chiefly a matter of complete hydrogenation. A sample of hydrogenated fish-oil fatty acids that was found satisfactory had an iodine value of 3, a titre value of 53°C. and contained 98 per cent free fatty acids. Experiments have shown that with an iodine value of 10 or less no fish-oil odour can be detected during the burning of hydrogenated fish oils or their fatty acids. Pilchard, herring, salmon or halibut head oils are suitable raw materials for this purpose.

Geller (1935) gives some data regarding candle manufacture. He states that candles can be divided into five groups as follows: Candles consumed in glasses or jars are made from scale or crude paraffin wax blended with stearic acid, or from a harder paraffin wax with a small amount of stearic acid. Better results are obtained with this type of candle if all the stearic acid is replaced by fully hydrogenated fats. These may be used up to 30 per cent of the total materials. The second group consists of coloured and decorative candles, which are usually made from a high-melting-point paraffin wax, to which is added from 5 to 10 per cent stearic acid. In the third group are the beeswax candles, which are used largely for religious purposes. These candles contain from 50 to 75 per cent pure beeswax, with which is blended a mixture of paraffin wax and stearic acid. The fourth group consists of household candles which are made from paraffin wax alone or admixed with stearic acid. The latter may be added in quantities up to 70 per cent

of the total mixture. Birthday and taper candles are the fifth group and usually consist of a high-melting-point paraffin wax with a small amount of stearic acid.

Recent patents dealing with candle manufacture show a very decided trend towards the use of hydrogenated fats or fatty acids. These are used in conjunction with paraffin waxes in amounts between 20 and 30 per cent. The hydrogenated acids do not have to be distilled, but can be produced from the hydrogenated fat by direct autoclaving or by any suitable saponification method.

(ii) CRAYONS

Stearic acid or hydrogenated fatty acids of low iodine value and titre of about 53°C. are utilized in the manufacture of crayons, either as a binder to cement the inorganic fillers and pigments together or as a solvent for certain oil-soluble dyes. In addition, such acids are used in the wax coat given to the leads of lead pencils. The following patents illustrate the use of saturated fatty acids in this field.

According to British patent 258,148, crayons or leads are made from dyes such as nigrosine dissolved in a mixture of stearine and carnauba wax or similar vehicle together with water soluble dyes and mixtures of clay, chalk or similar substances. British patent 461,109 describes how a crayon or water-colour paint is prepared by mixing together (1) vegetable oil and pigment, (2) clay and casein prepared from soya bean, and (3) vegetable wax and beeswax, this mixture being added to a mixture of hydrogenated fat, sodium hydroxide and water, and the final mixture being shaped and dried. Cellulose ethers are utilized, according to British patent 457,878, by mixing them with a filler, pigment and stearic acid, the mixture being ground, compressed, kneaded and pressed through dies to form a rod. After being cut to size the rods are dried and then soaked in a melted wax consisting of a mixture of stearic acid and carnauba wax. Yellow crayons can be made by following the directions of French patent 827,775, namely, by mixing together 20 parts of colophony, 15 parts of stearic acid, and 10 parts of yellow wax with 20 parts of chrome yellow. Canadian patent 357,438 describes how a filler and a pigment are united by a binder that includes a water-soluble etherized cellulose and a waxy substance composed of a mixture of stearic acid and wax. A similar patent is British 325,014, according to which ethyl cellulose or ester such as cellulose laurate derived from a fatty acid having at least 7 carbon atoms is dissolved at a raised temperature in stearic acid or mixtures of waxes containing the colouring material.

In all the above instances where stearic acid or stearine is used, the hydrogenated fatty acids from fish oil can be substituted provided that the iodine value and titre point correspond to the required specifications.

(iii) METALLIC SOAPS

The metallic soaps of saturated fatty acids as used in industrial work consist usually of the metallic salts of mixed fatty acids, chiefly palmitic, stearic and, to a less extent, myristic acid.

For many purposes these metallic soaps of mixed fatty acids are just as suitable as the metallic soaps of the pure saturated acids. In many cases, therefore, hydrogenated fish-oil fatty acids can replace commercial stearic acid as the raw material for making the metallic soaps of saturated fatty acids. It is impossible to list here all the uses that are made of such metallic soaps, but the following gives some idea of the wide range of application. Aluminium stearate is used in paints for flattening purposes and in varnishes and printers' ink to modify the flowing properties. It also has beneficial effects on the rust-preventing properties of paints. Aluminium stearate is used in certain types of lubricating greases and

along with calcium stearate has been suggested as a diluent for Paris green where it prolongs the effective period of dusting against insect attack. Mercury stearate is recommended as a bactericidal agent for treating paper money and copper stearate has been found to be an effective fly repellent. Aluminium, calcium and zinc stearates are used for waterproofing purposes and zinc palmitate has found use in leather finishes. A novel use of ferric stearate is the coating of metallic articles to prevent them from becoming wetted by oil during manufacturing processes. Zinc stearate is used in large amounts in pharmacy as dusting powder and is contained in many antiseptic preparations. Calcium and zinc stearates are also used as plasticizing and lubricating agents in the moulding of synthetic plastics.

(iv) MISCELLANEOUS

Many miscellaneous uses of saturated fatty acids could be enumerated. U.S. patent 2,126,128 describes a lubricant for use in metal drawing that consists of 65 per cent of a stearic acid of sufficiently high titre to provide a solid at 28° to 32°C., mixed with 35 per cent of mineral oil. Solid fatty acids, pitch and paraffin are used in the manufacture of fireworks as an agglutinant and to increase the mass and effect of the burning mixture. Manufacturers of buffing compounds and polishes are large consumers of stearic acid or its substitutes. These materials are also used for sizing paper for specialized uses.

The cosmetic industry is a large consumer of stearic acid, over 100,000 pounds having been used in Canada during 1938 exclusive of that used in soap manufacture. Practically all of this material is of the triple-pressed grade and conforms to the following specifications: saponification value 208, acid value 199, iodine value (maximum) 6, titre point 56°C. Hydrogenated fatty acids with these specifications can be made from British Columbia salmon oil; other fish oils give titre values about 53°C. However, as explained in Section 5 of this Bulletin, the titre point is not necessarily a fundamental criterion of quality and, if the iodine value is 6 or less, hydrogenated fatty acids with titre value about 53 should be acceptable. The chief concern of cosmetic manufacturers is that their stearic acid should be white, should contain but little unsaponifiable matter and, more important still, should remain colourless and free from odour when compounded into creams and stored for considerable lengths of time. Hydrogenated fish oil fatty acids can be made that are pure white; their stability depends upon the iodine value and the care taken in the hydrogenation process. Such fatty acids, when carefully made, are as stable as the best grades of stearic acid.

The soap industry is also a large consumer of stearic acid, the consumption in Canada averaging well over a million pounds. All grades are used, including single,- double- and triple-pressed, depending upon the product being made. Single- and double-pressed are, however, used in the largest amounts. Hydrogenated fish-oil fatty acids are suitable for most soap-making purposes where stearic acid is used.

(d) LIQUID UNSATURATED FATTY ACIDS

Under this heading are included the total fatty acids of fish oils and also the liquid unsaturated fraction that can be separated either by cooling and pressing or by steam or vacuum distillation.

(i) ORE FLOTATION

The separation and concentration of ores by flotation methods is a very specialized field of study that has only in recent years been put on a scientific basis. There are two chief types of reagents used in ore flotation, the frother and the promoter or the collecting agents. The function of the frothers is to build up a froth that acts as a buoyant medium, the ore to be separated being preferentially held by the bubbles whilst gangue sinks to the bottom of the treatment tank. Promoters or collectors are used to increase the floatability of the metal-bearing constituents of the ore; in other words, they make the frother more active, and in certain cases, more specific. Fatty acids and soaps belong to this second class of reagents, but, since they are only slighly selective, they are employed in places where specific collectors have not yet been found, chiefly non-metallics and oxide ores. Substances that can be floated with soaps or fatty acids without the addition of other activators include bauxite, hematite, calcite, ferberite, apatite, garnet, malachite and cerussite. Silica and silicates can be floated by these materials after the addition of a soluble metal salt. The separation from silicious matter of oxidized lead-ores can also be effected with fatty acids. Soaps of palmitic, oleic and stearic acids have been found to be very useful for separating oxidized copper ores, whilst palmitic acid is used commercially at the rate of 2 pounds per ton to concentrate an oxidized (carbonate) copper ore.

Although fatty acids and soaps are not listed among the most important of promoting and collecting agents, their use is gradually increasing, particularly in conjunction with accurate pH control. Oleic acid is probably the fatty acid most widely used, but other mixtures are also finding application in this field. Crude fatty acids from fish oil are used in very large amounts for the flotation of manganese ores in South America. Yu. V. and S. G. Branke (1937) have found that oleic acid, used for the flotation of ores in Russia, can be successfully replaced by fatty acids obtained from the stearine of sardine oil. These fatty acids are given a preliminary heat treatment, which may include mild blowing with air, and are then converted into their potassium soaps. These soaps were found to be as efficient as oleic-acid soaps when used for the flotation of manganese ores.

(ii) ALKYD RESINS

Fatty acids of both the drying and non-drying types are used to modify the properties of the resins formed by the interaction of glycerol or other polyhydric substances with phthalic acid or similar dibasic acids. Fatty acids produce a tougher and less brittle resin, and, if drying fatty acids are used, the resulting resin will have air-drying properties. Distilled unsaturated fatty acids from fish oils, which have an iodine value of 250 and a mean molecular weight of over 300, are now available commercially in the United States. The makers claim that

these fatty acids produce resins that have "excellent air-drying properties and are very similar to resins made with chinawood oil." In addition it is claimed that the tendency of the resin to gel during formation is less when these highly unsaturated fatty acids are used than when chinawood oil is employed. The use of alkyd resins made with highly unsaturated fatty acids in varnishes, paints and enamels causes rapid air-drying and the formation of a hard lustrous film. They are particularly recommended for baking enamels.

Several years ago the writer carried out some experiments on the use of pilchard-oil fatty acids as modifiers of alkyd resins. The fatty acids used were as follows: Series A, total fatty acids from cold-cleared pilchard oil; series B, liquid fatty acids from pilchard oil; series C, free fatty acids from steam-distilled pilchard oil; series D, free fatty acids from vacuum-polymerized pilchard oil; and series E, the total fatty acids from linseed oil. These fatty acids were used to replace a portion of the phthalic acid, each acid bring used in two proportions, namely 0.5 and 1.0 equivalents. The condensations were made at 210°C. (410°F.), the reaction being followed by acid-value determinations. When the reaction was completed, as indicated by constant acid values, the resins were plated out and their drying properties ascertained. In all cases the use of 0.5 equivalents of fatty acids with 2.5 equivalents of phthalic acid and 3 of glycerol gave the best results. Whilst the linseed-oil fatty acids gave the harder films, those made from pilchard-oil fatty acids were also satisfactory. The liquid fatty acids gave resins whose films were much harder than those of the total fatty acids and about two-thirds as hard as the linseed-oil resin films. The fatty acids of vacuum-bodied pilchard oil also yielded satisfactory resin films, the hardness approaching those of the linseed-oil resins. With the exception of the resins made with the total fatty acids of pilchard oil all the other fish-oil-fatty-acid resins had good gloss and in addition were definitely less brittle than those of the linseed-oil fatty acids. The fish-oil resins were not quite as fast in drying as those of linseed oil and took slightly longer to reach their maximum hardness.

(e) Minor Constituents of Marine Animal Oils

Uses for most of the naturally occurring *minor* constituents of marine animal oils have already received mention in the discussions of these constituents elsewhere in this Bulletin. The significance of the vitamins is amply covered in Section 3 I and in Section 9 I (b) and I (c); certain applications of the closely associated substances, pigments and sterols, have been pointed out in Section 3 II and III (a), respectively. Glycerol ethers and phospholipides, as directly obtainable from marine oils, have received relatively little attention from the standpoint of their technological uses; a few possible applications are mentioned at the conclusion of Section 3, III (b) and III (c). Marine animal waxes and the fatty alcohols directly obtainable from such waxes by saponification have definite recognized uses, which are summarized at the end of Section 3 III (d). Hydrocarbons, as a major constituent of certain shark liver oils, have applications that are referred to in Section 3 III (e).

Marine animal oils, fatty acids, fatty alcohols and hydrocarbons that have been subjected to chemical or other processes (e.g. hydrogenation, reduction of fatty acids to fatty alcohols, sulphation, sulphurization, halogenation, polymerization) give rise to such a great variety of products that any attempt to consider the utilization of these in detail would result in discussions outside the scope of this Bulletin. A number of uses for such processed products (e.g. sulphated oils and alcohols, page 138) are indicated in the appropriate divisions of Section 5 I and Section 8 II. The utilization of glycerol, obtained in large quantities from the hydrolysis and saponification of marine animal oils during soapmaking and other processes, is also considered as being beyond the scope of this Bulletin.

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SECTION 10. PROPERTIES OF SOME CANADIAN OILS

This Section of the Bulletin is devoted to a consideration of the more important marine animal oils available from either the Pacific or the Atlantic coasts of Canada. These are treated in three groups, the first including those fish and fish liver oils that are now produced commercially and for which production data are available. The second group includes miscellaneous fish oils which so far have not been produced in important commercial quantities. The third group embraces the oils from marine mammals. In order that the reader may assess the relative importance of each oil we have tried, where possible, to arrange our data to include (1) the biological classification, characteristics and abundance of the fish or mammal, (2) production statistics and type of fishery, (3) methods of production used, (4) properties and chief analytical characteristics of the oil, and (5) the chief uses of the oil. The analytical data are chiefly from our own laboratories. Where data from other sources are used these are duly acknowledged.

I. FISH OILS COMMERCIALLY AVAILABLE

This group includes body, liver, and visceral oils that are produced both as a primary product and also as a by-product of the fishing industry. They are listed roughly in order of their importance.

(a) PILCHARD OIL

The Canadian pilchard, *Sardinops caerulea*, is identical with the California sardine and belongs to the family Clupeidae, which includes the herring, shad and sardine. This fish spawns in an area roughly 200 miles in length and 100 miles in width, situated along the coast of southern California from San Diego to point Conception and offshore to a distance of 100 miles. The pilchards of British Columbia are merely the larger sardines that make a northward migration each summer. The larger the fish the farther northward do they migrate. Consequently, the British Columbia catch is more uniform as to size and age groups than the catch taken off the California coast. It seems fairly definite, therefore, that the Canadian pilchard stock is largely drawn from the main body of California sardines and the abundance of pilchards may be expected to follow that of the sardines. The importance of the fishery may be surmised from the fact that for the last four or five years it has supplied the industry with more than half a million tons of fish per year; the Canadian share of this catch amounts to between 5 and 10 per cent.

Dating from 1925 the commercial production of British Columbia pilchard oil assumed a place of some importance in the trade of the province. It reached

a maximum during the years 1926 to 1931, the peak being reached in 1928, as shown in table LXIV, with a production of almost four million gallons. In 1933 the catch was very small and for 1939 the figures so far available also show a very small production. During normal years, pilchards appear in considerable numbers along the west coast of Vancouver island from July to October, but, in poor seasons, they are taken in more southerly waters and fishing may continue till December.

TABLE LXIV. British Columbia pilchard and total fish oil production, 1926-1939

Year	Total fish oil (gallons)	Pilchard oil (gallons)	Year	Total fish oil (gallons)	Pilchard oil (gallons)
1926........	2,597,777	1,898,721	1933........	1,288,962	275,879
1927........	3,657,425	2,673,876	1934........	2,890,582	1,635,123
1928........	5,047,338	3,995,806	1935........	2,630,368	1,649,392
1929........	4,066,015	2,856,579	1936........	3,099,305	1,217,097
1930........	3,972,600	3,204,058	1937........	3,947,835	1,707,276
1931........	2,904,406	2,551,914	1938........	3,486,189	2,513,990
1932........	1,547,554	1,315,864	1939........	2,190,934	181,473

The fish are caught by purse seines and immediately transported to reduction plants where the entire fish are processed by the continuous system described in Section 7. The amount of oil in the fish varies with the season; during the earlier part of the summer the yield averages about 25 gallons to the ton (12 per cent), but towards the fall it increases to as much as 50 gallons to the ton. The oil thus produced is the raw pilchard oil of commerce.

Seasonal samples of pilchard oil for the years 1929 and 1937 analyzed in these laboratories failed to show any constant trend in characteristics with advance in season. From table LXV it is evident that in 1929 there was a

TABLE LXV. Seasonal variation in unsaturation (iodine value) of pilchard and sardine oils

Pilchard		Sardine (1937-1938)	
1929	1937	Northern area	Southern area
July 2 173.2	Aug. 1– 4 176.7	Aug. 16–21 185.0	Nov. 1 188.6
Aug. 2 177.3	Aug. 7–11 175.8	Aug. 22–23 186.8	Nov. 13 187.6
Aug. 9 179.3	Aug. 13–20 176.2	Aug. 23–Sept. 4 182.4	Nov. 27 189.5
Aug. 16 180.3	Aug. 23–Sept. 2 176.3	Sept. 5–11 187.3	Dec. 1 190.7
Aug. 16 181.9	Sept. 3– 7 173.0	Sept. 12–18 188.4	Dec. 28 182.8
Sept. 3 183.2	Sept. 7–14 177.0	Sept. 27–Oct. 2 189.5	Feb. 11 178.4
Sept. 15 183.4	Sept. 14–19 175.5	Oct. 3– 9 188.4	Feb. 22 176.1
Oct. 7 182.3	Oct. 13 178.2	Nov. 29–Dec. 4 188.5	Mar. 1 173.5
		Dec. 5–11 189.8	Mar. 8 185.3
			Mar. 11 181.1
			Apr. 14 170.9

regular increase in unsaturation from an iodine value of 173 on July 2 to one of 183 on September 3, but for the year 1937 no such trend exists. This lack of any definite trend in unsaturation is also borne out by the analyses of California sardine oil for 1937, although there is a slight indication of a lowering of the iodine value towards the end of the season in the southern area. The higher average unsaturation of sardine oil over that of pilchard oil is, however, quite marked. This feature is discussed in more detail in Section 2.

TABLE LXVI. Characteristics of pilchard, herring and salmon oils

Kind of oil	Pilchard	Brit. Col. herring	Salmon (commer.)
Sp. gr. at 25°C.	0.9140–0.9209	0.9135	0.9129–0.9231
Viscosity at 25°C. (poises)	0.46		
Colour (Lovibond units) yellow . .	16–30	1.5–20.0	15–30
red	1–3	0.1–1.2	1–25
Stearine (%, *at 13.5, **at 3°C.) .		2.3–11.4*	
Coeff. expans. (cc./cc./°C.)	0.00079		
Eth. insol. brom. glyc. (%)			36.4
Ref. index at 25°C.	1.4785–1.4802	1.4730–1.4775	1.4713–1.4802
at 40°C	1.4732		
Iodine value	170–188	118.0–159.7	110–177
Acid value	0.2–5.2	0.4–3.8	0.2–12.4
Sapon. value	188–199	182.0–189.0	182–193
Sat. fatty acids (%)		17.8–26.8	
Unsap. matter (%)	0.1–1.23	0.5–1.7	0.4–2.9
Vit. A (B.U../g.)	50–100	20–100	25–1000
Vit. D (I.U./g.)	20–80	20–80	30–230

As a result of analyses of samples of pilchard oil carried out in these laboratories over a period of ten years the limiting values of certain chemical and physical characteristics can be given. These are shown in table LXVI from which it can be seen that the greatest variation in chemical properties lies in the unsaturation, the iodine value varying from 170 to 188. The unsaponifiable matter varies over a small range. The colour range is much greater, depending to some extent on the nature of the feed of the fish. Although acid values as high as 5 have been found, these are exceptional, the average being much lower. The variation in vitamin content has been commented on in Section 3. In spite of the high unsaturation of pilchard oil, it deposits a fair amount of stearine at ordinary temperatures. The amount of the stearine and degree of unsaturation depend, of course, on the temperature at which the stearine is deposited. The commercial oil is also very low in nitrogenous matter, an average of 0.004 per cent nitrogen being found for several samples. This amount can be reduced by filtration or refining, as it is partly due to suspended matter. Analyses of four selected samples of pilchard oil are shown in table LXVII. No definite relationship between stearine content and iodine value has been found, but there usually exists an inverse relation between iodine value and quantity of total saturated fatty acids.

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TABLE LXVII. Typical analyses of British Columbia pilchard oil

	Sample produced Aug. 2, 1929	Composite sample produced, 1937	Sample produced Aug. 5-10/38	Sample produced Sept. 28/38
Stearine (% at 13.5°C.)....	....	17.0	24.8	29.5
Ref. index at 25°C	1.4785	....	1.4796	1.4792
Iodine value..............	173.2	177.2	180.9	172.3
Acid value................	1.1	....	2.5	2.3
Sap. value................	194.8	189.9	189.1	188.2
Sat. fatty acids (%)	....	21.9	19.5	20.2
Unsap. matter (%)........	....	0.4	0.4	0.4

The quality of the commercial grade of British Columbia pilchard oil is indicated in table LXVIII where analyses made on large bulk shipments show the low acidity and general freedom from impurities. Producers guarantee that shipments of pilchard oil will not have a free-fatty-acid content greater than 2 per cent and that moisture and insoluble impurities will not exceed 1 per cent. From these data it is clear that commercial pilchard oil is of uniformly high grade.

TABLE LXVIII. Average analyses of commercial pilchard oils

Season	Colour (1 cm. cell)		Moisture %	Ether insol. impurities %	Acid value
	Yellow	Red			
1928.............	..	..	0.35	Trace	0.9
1929.............	..	..	0.39	0.01	0.9
1930.............	..	..	0.26	0.02	0.6
1934.............	75.0	4.0	0.59	0.03	0.7
1935.............	58.0	4.0	0.21	0.01	1.1
1937.............	57.0	4.7	0.48	0.03	1.4
1938.............	59.0	4.6	0.36	0.02	1.1
1939.............	60.0	4.3	0.40	0.02	1.2
Ranges..........	40–75	3.5–6.0	0.09–0.66	Trace–0.04	0.6–1.8

The uses of pilchard oil have been considered in some detail in Section 9, but they may be summarized here. The oil is marketed in the raw state, and as light, medium and heavy pressed. The latter grades correspond to oils cold-cleared at 60, 50 and 40°F. respectively. Where the oil is to be used for its drying properties, heavy- or medium-pressed grades are used. This includes its use for paints, varnishes, oil-cloths, linoleum and felt-base floor coverings, water-proof cloths, core oils, putty, sulphonated oils, and oil-tanning of furs. Medium-pressed oils may be used for some of these and also for the preparation of shingle stains, structural steel and barn paints, sulphonating purposes and as a base for making poultry-feeding oils. Raw pilchard oil and the stearine from cold clearing are used for hydrogenation purposes, the products being utilized in foods, soaps,

and for the manufacture of fatty acids. The latter find use in lubricants, rubber manufacture, candles and similar materials.

(b) HERRING OIL

The herring, *Clupea pallasii*, caught along the British Columbia coast, is a member of the same family as the pilchard, the Clupeidae. The commercial value of this fish is almost entirely realized through conversion into fish meal and oil. The content of the latter, as explained in Section 2, is a variable factor dependent upon the sexual and/or nutritional condition of the fish. During the active-feeding period the oil content may be as high as 30 per cent, but it may drop to as low as 5 per cent after spawning. Practically all the herring caught in British Columbia waters are captured prior to spawning and thus the oil content decreases as the fishing season advances.

The following information regarding the seasons and localities of the herring purse-seine fishery of British Columbia was supplied the writers by Dr. A. L. Tester of the Pacific Biological Station of the Fisheries Research Board of Canada. Off the southeast coast of Vancouver island there is a fairly regular fishery which commences during the first part of October and continues into December, when the quota is usually reached. The runs on the west coast of Vancouver island are most erratic in time and occurrence. In the Barkley sound area fishing commences toward the end of October; in the Clayoquot, Nootka and Kyoquot sound areas in the middle of November, whilst in the Quatsino sound area it is December or later before the fishery commences. In the central British Columbia coast area, fishing has been carried on intensively only since 1936. The fishery is carried on from January to March and from September to November. In northern British Columbia the fishing season extends from November to March. In each of these areas the actual fishing dates may vary from year to year. All the areas mentioned are winter or spring fisheries, but a summer fishery was investigated off the Queen Charlotte islands quite recently. Whether this will prove to be commercially productive still remains to be seen. Due to apprehension regarding the possible depletion of the herring in each of the above mentioned areas (which seem to support their own population), definite quotas have been placed on each of them pending a complete investigation by the Pacific Biological Station.

All herring caught for fish meal and oil in British Columbia are processed by the continuous method described in Section 7.

The production of herring oil on the British Columbia coast within recent years has shown a marked increase. In the year 1930 there was a production of 60,373 gallons and in 1937 it reached 1,230,000 gallons, an increase of over 200 per cent. The following year, 1938, production amounted to 689,620 gallons, the decrease being attributed to a late season.

The herring of the Atlantic coast, *Clupea harengus*, is used principally for food and bait. The smaller herring, known as sardine herring, are canned in large quantities in southern New Brunswick, the pack being known as Canadian sardines. The offal from this cannery operation, together with fish too small or

otherwise unsuitable for canning, is put through a continuous reduction process and converted to meal and oil. Thus the total herring-oil production on the east coast of Canada comes from New Brunswick. In normal years the herring canning season commences about the middle of April and continues to the early fall. Recently, however, fishing and canning have been continued during the winter months. The total production of herring oil in New Brunswick averages about 30,000 gallons per year, although in 1934 it increased to 75,000 gallons.

Table LXVI contains a list of the general chemical characteristics and range of values of British Columbia herring oil, data derived from samples of oil obtained from various reduction plants and seining localities along the British Columbia coast and analyzed in these laboratories.

The oil expressed from the herring varies from a light yellow to a reddish brown in colour. It readily deposits large amounts of stearine at ordinary temperatures. Herring oil prepared from fresh fish usually has an acid value less than 1, but higher values have been found in oils produced just prior to spawning, when the oil is difficult to "break". The iodine value of this oil is lower than that of the pilchard or sardine and varies over a considerably wider range. Commercial herring oil has a low vitamin A potency, practically all of which is contributed by the liver; however, the small size of this organ, together with its relatively low oil content, have little effect on raising the potency of the total oil. The vitamin D values of herring oil have been found to be approximately twice as high as those of pilchard oil but slightly lower than cod liver oil.

TABLE LXIX. Local variation in unsaturation of British Columbia herring oil

Locality	Refractive index at 25° C.	Iodine value	Saturated fatty acids %
Butedale.......................	1.4749	141.7	19.2
Kyuquot sound..................	1.4743	140.3	20.0
Swanson channel (S.E. Vancouver is.).	1.4731	129.0	18.4
Barkley sound..................	1.4743	154.4	19.0

Herring oils produced in different localities along the British Columbia coast appear to show wide variations in unsaturation as indicated in table LXIX. These variations are not always reflected by changes in the saturated-fatty-acid content, nor are other analytical characteristics subject to the same degree of variation. It is not known at present how specific may be the degree of unsaturation of an oil from a definite locality, but in view of the probable existence of separate races of herring, and the fact that the fish caught in the various areas may be in different states of nutritional condition, it is probable that specific differences in unsaturation may actually exist.

In table LXX are given some data showing the average quality of bulk commercial shipments of British Columbia herring oil during the years 1936 to 1939. It is obvious from these figures that a high uniform quality is maintained

in the production of this oil. The percentage of free fatty acids is probably the most significant criterion of quality, and, although the values show considerable variation, even the highest value of 1.80 is very satisfactory for most industrial purposes. The variations in colour are most likely to be due to natural causes, since an oil that is darkened owing to improper processing usually shows a large increase in red colour. The average annual moisture contents are remarkably uniform but considerable individual variations are evident. The moisture content to a certain extent reflects the length of time and the temperature at which the oil has been tanked. It has but little significance in regard to the quality of dry oil.

TABLE LXX. Analyses of bulk shipments of British Columbia herring oil

	1936	1937	1938	1939
Average colour—yellow	25.0	21.3	29.3	20.7
—red......	2.5	2.3	2.3	2.5
Colour range—yellow......	23.0–27.0	21.0–22.0	25.0–35.0	20.0–25.0
—red........	2.1–2.7	1.8–3.4	2.2–2.4	2.0–3.2
Average moisture	0.31	0.57	0.46	0.33
Moisture range...........	0.12–0.52	0.25–0.80	0.31–0.54	0.09–0.65
Ether insol. mat. (%)......	0.01	0.01	0.01	0.01
Average acid value.	1.30	1.06	0.89	1.04
Acid value range.........	0.56–1.80	0.77–1.41	0.77–1.02	0.63–1.34

Several samples of commercial Atlantic coast herring oil have been examined in these laboratories. Most of these were of a rather dark colour and strong odour. The acid values were higher than those found for Pacific coast herring oil. One or two experimental lots of Atlantic coast herring oil have also been examined. These were of excellent quality, being light in colour, low in free fatty acids and moisture, and practically free from odour.

The low unsaturation and high stearine content of herring oil prevent the rapid absorption of oxygen, and on account of this, films of herring oil do not dry satisfactorily. For this reason, the use of herring oil in the paint and varnish industry is limited. However, this slow-drying characteristic, and the adhesive quality of the oxidized oil, have proven to be assets in the manufacture of insecticides, particularly for tree banding and for the spray control of the codling moth on fruit trees. The high stearine content of this oil makes it a valuable raw material for the production (by hydrogenation) of "stearic acid", which readily finds a market in the various candle, cosmetic, rubber, leather and lubricating industries. Also by hydrogenation herring oil is converted into a form in which it can be used in the manufacture of soap and edible shortenings. The introduction of this oil as a lubricating grease is fairly recent and it has been found satisfactory where heavy-duty cutting oils are in demand. Another recent innovation is the use of fish oils in sheep dips and there is some possibility that herring oil might be applied in that field. The vitamin potency and the relatively low cost of this oil appeal to those who are interested in the field of poultry and animal

husbandry.   However, the high stearine content necessitates adequate cold clearing, judicious blending with non-freezing oils or the addition of some stabilizing substance.

(c) SALMON OIL

Unlike pilchard and herring oils, the commercial salmon oil of British Columbia is not a product of the whole fish but a by-product of the salmon canneries and salteries operating on the five species of salmon (*Oncorhynchus*) indigenous to this coast.   For information regarding the biological character and abundance of these fish the reader is referred to the many publications of the Pacific Biological Station of the Fisheries Research Board of Canada dealing with the life-history and propagation of Pacific salmon.

The most comprehensive study of Pacific salmon oils has been made by Harrison *et al.* (1939), of the United States Bureau of Fisheries, and whilst this study was based on Alaska and Columbia river salmon many of the data are directly applicable to British Columbia salmon oils.   The subject of salmon oil production naturally begins with the amount of offal available for processing. Harrison *et al.* give data for the five species which are shown in table LXXI.

TABLE LXXI.   Salmon offal statistics (Harrison *et al.* 1939)

Species	Spring	Sockeye	Pink	Coho	Chum
Offal per case of 48-lb. canned fish (lb.)	20.5	23.6	25.8	23.6	23.6
Oil per ton of offal (U.S. gal.)	30–40	25–35	15–25	12–18	10–15

These figures represent the total amount of salmon waste per case of salmon produced at the cannery, and the respective oil contents of such waste.   The data of British Columbia salmon canners would show that the above figures are approximately correct since it is recognized that for sockeye, springs and coho it requires from 75 to 76 pounds of fish to make one 48-lb. case of the canned product.   The amount required is higher for chums and pinks.   This means that for every case of salmon canned on this coast there is *at least* 27 lb. of waste material produced.   Applying the data of Harrison *et al.* to the packs of British Columbia salmon for the years 1934 to 1938 the startling figures shown in table LXXII are obtained.

According to these data, even though the production of salmon oil has increased markedly during the past few years, only slightly more than half of the possible production has been realized.   A consideration of some of the sources of loss, and errors in calculation are therefore of some interest.

Data obtained from a reduction plant operating on the offal of a number of near-by canneries, show that the estimated amount of offal per case of salmon packed is very much smaller than the above figures would indicate.   For instance, for sockeye and pink salmon the number of pounds of offal per case is estimated as between 8 and 12 lb. per case.   The oil yields for sockeye and pink salmon offal are found to be within the range given by Harrison *et al.*, but that for chum salmon offal is much smaller, namely 7 gallons per ton.   There is thus a great

Kind		1934	1935	1936	1937	1938
Spring	Canned product (cases).....	29,784	21,920	29,854	16,171	15,052
	Calculated oil (gal.)........	· 9,190	6,764	9,212	5,000	4,645
Sockeye	Canned product (cases).....	377,882	350,444	415,024	325,774	439,698
	Calculated oil (gal.).........	113,364	105,134	124,508	97,732	131,910
Pink	Canned product (cases).....	435,634	514,966	591,532	585,576	398,847
	Calculated oil (gal.)........	84,395	99,826	114,668	113,514	77,316
Coho	Canned product (cases).....	225,430	231,492	246,061	133,208	305,453
	Calculated oil (gal.).........	67,629	69,448	73,818	39,962	91,636
Chum	Canned product (cases).....	513,184	409,604	598,487	447,602	537,087
	Calculated oil (gal.)........	61,582	49,152	71,698	53,712	64,450
Total calculated oil..................		336,160	330,324	393,904	309,920	369,957
Oil actually produced................		123,641	61,313	171,326	169,239	194,448
Percentage of calculated yield........		36.8	18.6	43.5	54.6	52.6

loss of offal between that produced at the cannery and that received at the reduction plant. Some of the circumstances contributing to this loss may be enumerated. The canning of tips and tails and other edible portions of the fish left by the iron chink, whilst not being a general practice in all canneries, undoubtedly reduces the total offal available in some plants. The large amount of water used to flush the offal from the iron chink tends to make a very fluid mixture in the offal bin. These bins are never water-tight, and it is the opinion of some operators that a great deal of the loss occurs at this point, the water washing away oil and soluble proteins. This is particularly noticeable if the offal is not removed immediately, autolytic and bacterial action increasing the amount of liquid products that are lost through the floor of the bin. It is also a fact, that the yield of offal per case of salmon packed is higher in those reduction plants that are operated in conjunction with a cannery, than in those that are situated some distance from the cannery and which, therefore, cannot get the offal in as fresh a condition. Similarly, it has been observed that in a particular case of a reduction plant operating at some distance from the canneries supplying the offal, and where the latter could be collected daily and therefore in good condition, the amount of offal per case of fish packed was higher than when the offal was collected only once or twice a week. This circumstance emphasizes another practical point, namely the distance of the cannery from the reduction plant. In the above table of calculated yields, it was assumed that all the offal from all canneries would be used. At the present time this is not feasible, as some canneries are situated in isolated spots many miles from a reduction plant and the cost of transportation of the raw offal would be prohibitive.

It has been found by actual experience that it is not profitable to operate a reduction plant exclusively on salmon offal, and those that do operate on this material have been installed primarily for the reduction of herring and pilchards. It is therefore necessary to use the same processing system for salmon offal, but the continuous systems now employed satisfactorily for herring and pilchards

will not handle the viscera and spawn in salmon offal which, it is claimed, makes up about 50 per cent of the total offal. The use of other methods, particularly designed for salmon offal, is restricted by the fact that the great bulk of the offal is produced within the short space of 6 weeks, and in order to handle the large quantity of material in such a short time the capacity of such equipment would have to be very large. It would then stand idle for the rest of the year unless such modified equipment could be utilized for pilchard and herring reduction. The problem seems to resolve itself into the elaboration of such a method of treating the raw offal at the cannery that the semi-processed material will not spoil, and therefore can be transported economically to central reduction plants for the final conversion into meal and oil. As far as the writers are aware, no entirely satisfactory method has yet been devised. Among the many methods suggested mention may be made of the treatmen tof the offal by chemical preserv-atives and coagulants, sterilization and partial drying of the offal by waste or off-peak cannery steam, and the recovery of oil alone from the segregated viscera by alkali digestion. The latter suggestion has the merit that the removal of the viscera from the bulk of the offal facilitates the treatment of the latter in the continuous reduction plants. Should the value of salmon meal and oil be increased, these methods will doubtless receive serious consideration by the industry.

Commercial salmon oil is quite highly pigmented, its colour ranging from a cherry red to a light amber, depending upon the species of fish, and upon whether total waste or selected parts of the waste are used. The oil from the eggs is usually the most highly pigmented whilst that from the liver is the least. The most highly pigmented oils are obtained from coho and sockeye salmon; the least pigmented are from chum and pink. Other fish oils such as pilchard and herring normally have but little red in their colour composition. If increased red colour is produced by oxidation during manufacture, these oils are of much less com-mercial value, since this red colour adds to the difficulty of subsequent refining. The red and a part of the yellow pigment of salmon oil, however, can be removed by treating with bleaching earths or by alkali-refining. In the former case the pigment is apparently destroyed, but in the latter it is merely adsorbed by the settling soap and can be recovered. In a typical decolorizing experiment 400 grams of commercial salmon oil was heated on a water bath to 98°C. (208°F.) and then intimately mixed for 5 minutes with 30 grams of an activated British Columbia bentonite. The mixture was immediately filtered through a suction filter and the colour determined in Lovibond units with the results that "yellow' was found to be reduced from 29.9 to 7.0 and "red" from 9.0 to 0.5. The red pigment is more unstable than the yellow. When a red salmon oil is heated to 140°C. (284°F.), the red pigment disappears rapidly. In the presence of oxygen it is very unstable even at low temperatures. This pigment may be destroyed by conditions that do not alter the other characteristics of the oil. In one experiment a deep-red salmon oil was heated rapidly to 140°C. and in 2 minutes

the red colour had disappeared, but there was no change in iodine value of the oil. The red colour is also removed in the early stages of the process of hydrogenation.

Other ranges in the general characteristics of commercial salmon oil, besides colour, are shown in table LXVI. The maximal limit of the free fatty acid content is noticeably higher than that obtaining in pilchard and herring oils, owing to the processing difficulties already mentioned. Considerable variation is likewise evident in the unsaturation of commercial salmon oil, as shown by the iodine values and refractive indices. This is due not only to the number of different species used for the production of the commercial oil, but also to the fact that the oils from fish of the same species, caught in different localities, vary among themselves. The variation in properties of oils obtained from the different species is evident from table LXXIII, which was compiled from the work of Harrison *et al.*

TABLE LXXIII. Characteristic ranges in properties of oils from various species of salmon (Harrison *et al*, 1939)

	Chinook or spring	Sockeye	Pink or humpback	Coho	Chum
Sp. gr......	0.9129–0.9183	0.9179–0.9210	0.9200–0.9231	0.9180–0.9225	0.9201–0.9221
Ref. ind....	1.4713–1.4758	1.4760–1.4780	1.4779–1.4802	1.4744–1.4797	1.4780–1.4792
Iodine val..	111–144	148–160	168–177	159–172	155–162
Acid val ...	0.2–2.6	0.3–2.4	0.3–0.4	0.5–2.4	0.9–2.3
Sap. val....	187–191	183–187	183–190	182–188	184–186
Unsap. (%).	0.9–2.7	1.1–2.7	1.0–2.4	1.7–2.8	2.2–2.9

As pointed out by these authors it is noticeable that those species having the shortest life cycle yield the most highly unsaturated oils. Oil from the viscera is more unsaturated than body oil, whilst egg oil is extremely unsaturated, some samples having an iodine value of 220. In view of these facts it will be readily appreciated why salmon oils vary in classification from the non-drying to the semi-drying class. On the basis of their chemical characteristics, pink-salmon and coho-salmon oils are comparable to Atlantic menhaden oil, sockeye- and chum-salmon oils to herring oil, whilst spring-salmon oil is even less unsaturated than herring oil.

Not only does the unsaturation of salmon oil vary with species and locality, but there is also considerable variation in the nature of the oil from the various fat depots of the fish. This has been extensively shown by Lovern (Section 2) for a number of fish, and by the present writers for coho salmon. In table LXXIV are given data, compiled from our analysis of eight different fat depots in this fish, which show that selective deposition undoubtedly does take place. The liver oil is noticeably more unsaturated than most of the storage fats, as reflected by the high iodine value and the low content of saturated fatty acids. This is in direct contradiction to the findings of Lovern for other fish, but may be partly explained for salmon by the liver not being an important depot for fat storage.

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TABLE LXXIV. Analyses of oil in fat depots of coho salmon

Source of oil	Iodine val.	Sap. val.	Sat. F.A. (%)	Unsap. (%)
Whole head.....................	160.7	212.7	13.3	2.70
Head, outer muscle.............	145.3	186.6	13.7	2.09
Head, inner muscle.............	149.1	192.8	15.1	2.16
Dark muscle....................	154.5	191.6	12.3	1.58
Tail, inner muscle..............	148.8	189.9	15.8	3.09
Skin...........................	154.5	190.4	17.1	1.54
Egg (acetone-sol.)..............	220.3	180.4	11.5	6.08
Egg (acetone-insol.)............	151.0	201.7	11.1	2.28
Liver..........................	167.0	200.1	8.7	9.15

The highly unsaturated nature of salmon liver oil was well shown by Bailey (1934) of these laboratories, who found in examining several different samples of oil from all species, that the average iodine value was 207.2.   The high iodine value and relatively high saturated-fatty-acid content of the true glyceride portion of the egg oil would seem to indicate the presence of a fair amount of very highly unsaturated fatty acids.   The skin oil and dark-muscle oil are more unsaturated than the oil from muscle nearer the bone; this has been found to be true of other salmon.   The total head oil appears to be more highly unsaturated than either of the constituent depots examined, which would lead to the conclusion that there must be a depot in the head where very highly unsaturated oil occurs. Variation in deposition of storage fats in salmon was likewise found for ten red spring salmon examined in these laboratories. These data show that almost invariably the oil from the pink muscle is more unsaturated than that from the dark muscle; also that the oil from the flesh near the head is more unsaturated than that from near the tail.

Salmon oil is readily oxidized.   From analytical data obtained in these laboratories it was found that, when red-spring-salmon oil was subjected to continuous blowing with air at 100°C., the degree of unsaturation steadily decreased, whilst the viscosity and molecular weight increased.   The final product was very viscous but did not gel.   It had an oxidized fatty-acid content of 13.8 per cent. Raw salmon oil exposed to the air never dries to a non-tacky film; samples exposed for several months became thick and viscous, but were always of a fluid nature.

TABLE LXXV. Rate of hydrogenation of commercial salmon oil

Period (min.)..........	0	30	50	85	110	180	270	900	1200
Titre (°C.)............	25.28	24.48	26.52	37.98	46.38	50.17	55.84	55.83	55.62
Iodine value..........	141.3	116.3	81.1	58.5	37.8	27.4	3.6	1.4	0.8

When hydrogenated, salmon oil forms a white odourless fat.   It submits to the process of hydrogenation quite readily, as shown in table LXXV.   A concentration of 0.7 per cent nickel catalyst was used.   It is to be noted that the

final sample of the saturated fatty acids give a titre test of 55.6, which is higher than that usually obtained for other British Columbia fish oils.

Salmon oil finds industrial uses in three distinct fields. By reason of its vitamin potency, discussed in greater detail in Section 3, it is of considerable value as a poultry-feeding oil. Up to the present, only small quantities have been utilized for this purpose but in view of the increasing demand for animal-feeding oils and the inadequate supply of cod liver and similar oils it is likely that salmon oil will find greater use in this field. Commercial salmon oil is also a very satisfactory oil for sulphonating purposes and, as far as the leather industry is concerned, has a preference over certain other fish oils for particular types of leather manufacture. Finally, as noted above, the fatty acids of fully hydrogenated salmon oil are pure white and have a titre of over 55°C. Certain industries require solid fatty acids with titres approximately 56°C. and these can be supplied from salmon oil.

(d) Cod Liver Oil

Codfish (family Gadidae) are caught on both coasts of Canada but the fishery on the Atlantic coast is of much greater importance. In 1937 the Canadian Atlantic cod fishery produced 1,509,320 cwt. of dressed fish valued at $3,097,278. The latter included $30,122 worth of medicinal cod liver oil at 55 cents per gallon and $46,316 worth of "cod oil" at about 38 cents per gallon. This important fishery is carried out in all four of the east coast provinces, Nova Scotia being the greatest producer, followed in turn by Quebec, New Brunswick and Prince Edward Island. The fish, *Gadus callarias*, is caught chiefly from May to September but certain banks are fished practically through the entire year by some of the large trawlers. A quantity of medicinal oil is produced aboard these vessels, but, in Quebec and Prince Edward Island particularly, oil is also made in small shore establishments.

TABLE LXXVI. Canadian and Newfoundland production of cod liver oils in gallons

Year	Canada		Newfoundland	
	"Cod liver oil"	"Cod oil"	"Cod liver oil"	"Cod oil"
1931.............	51,651	142,733	118,487	928,000
1932.............	38,721	111,228	158,538	645,376
1933.............	57,710	137,376	184,641	669,473
1934.............	52,958	113,376	169,123	556,149
1935.............	60,570	93,913	195,147	566,104
1936.............	70,488	89,811	265,952	791,824
1937.............	49,624	122,822	......	......

The total Canadian production for the years 1931 to 1937 is given in table LXXVI, in which are also included, for comparison, the export figures for cod liver oils from Newfoundland. From these data it will be seen that the Canadian production of "cod liver oil" is between one quarter to one third that

of the Newfoundland production. The ratio of "cod liver oil" to "cod oil" production in Canada ranges from 1.2 to 2.8, whilst for Newfoundland it ranges from 2.9 to 7.8. This means either that the Canadian producers get a higher yield of medicinal oil from the livers, or that in Newfoundland livers other than cod are used in the production of the low grade "cod oil." Another interpretation may be that under the close government supervision obtaining in Newfoundland and the single-boil single-skim method of production in vogue, the proportion of high-grade medicinal oil produced is lower than where other methods are used. It would appear, however, that the Canadian production of "cod liver oil" could be increased. MacPherson (1937) states that in Newfoundland it is estimated that 450 lb. of fresh fish or 320 lb. of dressed green fish are required to produce 1 gallon of first grade oil. On the basis of these figures, and whilst admitting that they may not directly apply to the Canadian production, it can be estimated that in 1937 at least 300,000 gallons of first grade oil could have been produced. The reasons for the low production are, of course, the low price paid for non-tested medicinal oil and the scattered area over which codfish are landed. Several suggestions have been made as to how a better price can be obtained for the small individual oil producers, but to date none of these has been adopted. In any scheme where oil is to be collected from small producers two things are essential, namely, a uniform simple method for the extraction of first quality oil from fresh livers and an adequate number of collecting centres where the oil can be clarified, wintered and stored until sufficient quantity has been accumulated to warrant the expense of a vitamin assay. Medicinal cod liver oils today must be of a guaranteed vitamin potency in order to enjoy a steady market and the assay, on account of its cost, must be made on as large a quantity of oil as possible. Methods of production that are available for the small producer have already been discussed in Section 7 and in this regard the apparatus of Labrie and co-workers seems to have merit.

The effect of various methods of production on the quality of the oil is very well brought out by analyses made by the writers on a number of representative samples of cod liver oil collected for us by Inspectors of the Department of Fisheries during 1938. In order to show the wide variation in quality as indicated by certain analytical characteristics the results of the analyses of some twenty samples are given in table LXXVII. The difference between sun-rendered samples and those prepared by the steam process is very marked. The former samples are characterized by high acid values and dark colour. Usually, they possess a bad odour. The first-run samples from the steam process are uniformly of high grade as far as acidity and colour are concerned. The range of unsaturation as shown by the iodine values is greater than that found by Holmes and Clough (1927) for over a hundred samples of oil from the eastern North American coast. Other characteristics, such as unsaponifiable matter, saponification values, etc. (only done on selected samples and not shown in the above table) fall well within the ranges noted by Holmes and Clough. The vitamin A potencies of a few of the samples, as shown by the blue values, vary

over a considerable range but, since insufficient data are available regarding the size of the fish used and yield of oil obtained for these samples, little significance can be attached to the values. They do emphasize, however, the necessity of blending the oils to obtain a more or less standard potency, and the desirability of a thorough investigation into the fluctuations of the vitamin potency of Canadian cod liver oils.

TABLE LXXVII. Some properties of Canadian Atlantic cod liver oils

Description of sample	Colour units		Iodine value	Acid value	Vitamin A, (B.U./g.)
	Yellow	Red			
Prince Edward Island,					
steam proc., No. 1...	3.9	0.2	121.8	1.05	
No. 2...	3.5	0.2	118.3	6.8	
Prince Edward Island,					
steam proc..........	1.7		134.2	0.4	1500
Nova Scotia,					
steam proc., no. 1 ...	3.2		147.3	0.2	
no. 2 ...	9.1	1.0	167.6	7.7	
Nova Scotia,					
steam proc..........	2.5	0.3	154.4	0.2	
	3.0	0.3	160.8	1.3	800
	2.6	0.1	154.8	0.2	..
poultry grade..			175.7	0.8	260
Magdalen islands,					
steam proc.............			164.9	0.3	500
Nova Scotia,					
steamed at sea.........	3.0	0.2	186.5	0.5	120
Nova Scotia,					
steam proc., wintered....	3.5		173.8	0.5	200
Prince Edward Island,					
stove rendered.........			144.6	1.2	50
Nova Scotia,					
cod oil cookers.........	3.0		153.0	1.5	
Prince Edward Island,					
sun rendered...........	28.0	4.0	143.6	37.2	
	>30	>30	131.2	51.9	
	>30	>30	121.1	54.8	
	20.0	>30	128.3	44.8	300
commercial poultry.....	20.0	15.0	148.6	18.9	680
Nova Scotia,					
Wentworth proc., no. 1 .	2.6	0.2	156.7	0.7	1850
no. 2 .	9.0	1.0	162.5	9.5	

In table LXXVIII are given some ranges of analytical values of "cod liver" and "cod oils" manufactured on the Atlantic coast. They were compiled from the data of Holmes and Clough (1927), Holmes, Clough and Owen (1929) and from values found in our own laboratories. The data indicate what variations might be expected in these oils.

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Table LXXVIII. Oils from Pacific and Atlantic cod

	Pacific cod		Atlantic cod	
	Liver	Viscera	"Cod liver oil"	"Cod oil"
Per cent in fish............	3.0	3.3		
Per cent oil..............	31.2	2.4		
Oil analyses				
Sp. gr. at 25°C..........	....	....	0.920–0.927	0.919–0.926
Colour (Lovibond units)Y.	10–14	....	1–4	3–40
R.	....	....	0.1–0.3	1–40
Ref. index at 25°C.	1.477–1.480	....	1.4772–1.4813	1.4765–1.4830
Iodine value............	150–185	145	121–186	118–167
Acid value..............	1–10	....	0.2–2.3	3.5–54.9
Sap. value..............	183–185	....	182–191	185–195
Sat. fatty acids (%).....	17–18	....	17.3	....
Unsap. matter (%)......	1–3	10.5	0.9–1.4	1.2–2.8
Vit. A, (B.U./g.)	1,000–20,000	28,000	.....	.....
Vit. D, (I.U./g.)........	85–1,000	35	.....	.....

"Cod liver oil" finds its greatest use in human nutrition. A great deal of it is used for making vitamin A and D concentrates whilst the lower grades are used in animal nutrition. Some "cod oil" is also used for the latter purpose but the greatest outlet for this oil is in the tanning industry, which for many years has looked upon "cod oil" as the material par excellence for certain types of leather manufacture. On account of its specialized use in this field little endeavour has been made to find other uses for it. Up to the present time, however, it has brought a better price for tanning purposes than it would for other uses that might be suggested for it. Like other fatty oils, "cod oil" can be hydrogenated, but the commercial grades require extensive refining before the process can be applied successfully.

The codfish of the Pacific coast is the grey cod or Alaska cod, *Gadus macrocephalus*, which is fairly abundant in the waters from Puget sound to southeastern Alaska. The fish may be taken throughout the year, but is more abundant from October to March. Only small landings are made in British Columbia, most of the fish caught being sold on the local fresh fish markets or used for halibut bait. The landings in 1937 amounted to 1,430,600 lb. The flesh of the grey cod is non-oily, but the livers, which constitute from 2 to 4 per cent of the weight of the fish, contain from 15 to 40 per cent oil (Pugsley 1939). There appears to be no relation between the oil content of the livers and the weight of the fish, but it was observed that the oil content increased during the fall and winter months. The average content of viscera and liver of over 200 fish caught over a 12-month period, together with the per cent oil and oil analyses, are shown in table LXXVIII.

The average yield of oil from the Pacific cod is lower than that from the Atlantic. The oil has the same range in unsaturation, but is more highly pig-

mented and has a higher content of unsaponifiable matter. The vitamin potency is slightly higher than for the Atlantic cod but is subject to greater variations. A composite sample of grey cod intestinal oil showed a lower unsaturation than the liver oil, higher unsaponifiable matter, high vitamin A potency but low vitamin D content.

(e) HALIBUT OILS

Halibut are common to both the Atlantic and Pacific oceans. They are members of the Pleuronectidae, a large family of flatfishes, but belong to different species. The Pacific halibut, *Hippoglossus stenolepis*, is widely distributed, being found from San Francisco, California, up the coast to the gulf of Alaska and Aleutian islands. Its fishery is regulated under an international agreement between Canada and the United States and the annual quota has been set at about 46 million lb. The average yearly landings of the Canadian fleet approximate 11 million lb.

The Atlantic halibut, *Hippoglossus hippoglossus*, differs slightly from the Pacific species but has similar habits and life history. In the western Atlantic its distribution is similar in latitude to that on the Pacific coast, ranging from New Jersey northward to the coasts of Nova Scotia, Labrador and Davis straits. The Canadian Atlantic landings of this fish amounted to about 3.5 million lb. in 1937.

In this fishery there is very little waste. The fish are eviscerated at sea but the heads are left on until landed at port. The livers are iced down and sold to dealers for about 50 cents per lb. The viscera are saved by some fishermen and bring 10 cents per lb. In 1938, $126,000 worth of halibut livers and $37,000 worth of intestines were landed in Prince Rupert, B.C. When a load of halibut is sold, the heads are taken off and these are removed to a reduction plant where they are converted into fish meal and halibut head oil. There are thus three kinds of oil commercially available from the halibut fishery.

(i) LIVER OIL

This is produced from the raw or frozen livers by methods outlined in Section 7. Some characteristics of the oil are given in table LXXIX. The livers are of a reddish grey colour and range in weight from 0.95 to 1.45 per cent of the total weight of the fish. According to Pugsley (1939), the oil content of the livers varies between 11 and 30 per cent, and in general the oil content tends to be higher during the summer months than during the spring and fall. The oil from fresh livers is of a lemon yellow colour (depending largely upon the method of extraction) and possesses a slightly fishy odour. The unsaturation is not very high but varies over a considerable range. Haines and Drummond (1934) claimed that there is a direct relationship between the iodine value of halibut liver oil and the amount of vitamin A present. In these laboratories, Pugsley (1939) could not confirm these findings, but found that there was some relationship between the unsaponifiable content and vitamin A potency. A simple

TABLE LXXIX. Characteristics of halibut oils

Source	Liver	Head	Viscera
Colour (Lovibond units) yellow.	10.5	2.3–2.7	10–20
red....	1.3		12–30
Ref. index at 25° C.	1.4817–1.4886	1.4757–1.4768	1.4912–1.5000
Iodine value.................	121–153	137–150	144–167
Acid value..................	0.1–1.7	0.6–2.3	2.7–10.0
Sap. value...................	166	187	143–147
Sat. fatty acids (%)	15–16	25	15–16
Unsap. matter (%)...........	5–16	0.8	16–23
Vit. A (B.U./g.)	8,000–200,000	60–100	20,000–400,000
Vit. D (I.U./g.)	1,000–5,000	5–10	100–500

calculation will show that the variation in vitamin A potencies commonly found in fish liver oils is not great enough to explain the variation in iodine values, an increase in vitamin A potency of 50,000 units affecting the iodine value by only about 2 units. Any relationship between vitamin A potency and unsaturation must, therefore, be due to some other unsaponifiable matter accompanying the vitamin A. Further discussion of the vitamin potency of halibut liver oil will be found in other sections dealing with vitamins and their sources.

(ii) HEAD OIL

This is produced by the continuous reduction process from the halibut heads collected from fresh and frozen fish establishments. The heads constitute from 10 to 12 per cent of the weight of the fish and have an oil content ranging from 10 to 20 per cent. In the reduction plant, halibut head oil is usually found to be mixed with salmon oil since the dealers handling halibut also handle fresh salmon and the heads are mixed indiscriminately. However, samples of pure halibut head oil have been produced commercially and many samples have been made in these laboratories. The commercial production of this oil during 1939 was but 8,000 gallons.

Some of the characteristics of halibut head oil are shown in table LXXIX. It is a clear pale yellow liquid that deposits but little stearine in spite of its relatively low unsaturation and high content of saturated fatty acids. The iodine value of samples examined in these laboratories over a period of years has shown a variation of only about 13 units. It is low in unsaponifiable matter and contains but little vitamin A or D.

Halibut head oil does not readily absorb oxygen, and it does not oxidize to a dry film but remains thick and viscous. This adhesive characteristic, which prevents its use in the protective coating industries, is of value when the oil is used for insecticide sprays and for tree-banding compounds. The low content of unsaponifiable matter warrants the use of the oil in the hydrogenation process and the hardened oil (or its fatty acids) makes a good substitute for commercial stearic acid. The oil can be sulphonated and the product used as an emulsifier and fat-liquoring agent in the leather industry.

(iii) VISCERAL OIL

This has been a commercial product since the fall of 1937. Pugsley (1939) found that the viscera, which include the spleen, intestines and adjoining glands, are responsible for about 2 per cent of the weight of the fish. The oil content is very low and ranges from 1 to 5 per cent. There appears to be no seasonal fluctuation in the oil content, as found for the livers of this fish, nor any increase in the per cent in relation to the increase in weight of the fish. Data obtained from numerous analyses made on this oil are given in table LXXIX.

Halibut visceral oil is of a medium reddish-brown colour with a rather unpleasant acrid odour. This odour can be improved by suitable high-vacuum deodorization methods. The oil is slightly more unsaturated than halibut liver oil but the range of unsaturation is not so great. The acid values vary greatly with the age of the viscera and with the method of extraction. All the values reported in the table were obtained on oils made by alkali extraction from "fresh" viscera, but even so the acid values may be as high as 10. Oils made from stale viscera by solvent processes may have acid values as high as 60 or 70. The unsaponifiable matter is very much higher than that found in the liver oil and this may in part account for the high refractive index. It has been found that the vitamin A content of the visceral oil varies directly with the weight of the fish. Further details on the vitamin potency of this oil will be found in other sections of the Bulletin.

(f) LING-COD LIVER OIL

Ling cod, *Ophiodon elongatus*, commonly known as cultus, blue cod and buffalo cod, is related to the greenlings and sculpins. These fish have a fairly wide distribution along the Pacific coast ranging from Alaska to point Conception, California. In the southern waters the fish are smaller and not nearly so plentiful as they are in British Columbia waters. They are caught throughout the year but the heaviest catches are taken during the months of February, March, April, August, September and October.

Ling cod is considered the most important of the minor fisheries on the Pacific coast and has attained fifth position in value amongst the food fishes of British Columbia. The average yearly landing over the past five years is 5,254,200 lb., practically all of which is sold on the fresh fish market. In 1933, during the course of a general survey undertaken by these laboratories on the vitamin potency of British Columbia fish oils, it was found (Bailey 1933) that the livers of the ling cod, which up to that time were being discarded, were a valuable source of vitamin A. However, since that date an average of 59,000 lb. of ling-cod livers has been landed annually for oil processing. This amount is equivalent to approximately 518 gallons of liver oil.

The fish caught in these waters are very large, ranging in weight from 30 to 40 lb. The liver constitutes 1 to 4 per cent of the total weight of the fish. The oil content of the liver is from 5 to 10 per cent whilst that of the flesh is low, approximately 1 per cent. Oil produced from fresh livers by suitable methods

is of a light yellow colour and possesses a slightly fishy odour. The unsaturation varies over a considerable range, similar to that found for halibut liver oil.

The unsaponifiable matter rarely exceeds 10 per cent and usually averages slightly over 5 per cent. The saturated-fatty-acid content falls within the range commonly found for fish liver oils. Table LXXX presents a list of the general chemical characteristics and range of values; data obtained from samples of ling-cod liver oil produced at these laboratories.

TABLE LXXX. Characteristics of ling-, red-, and black-cod liver oils

	Ling cod	Red cod	Black cod		
			Liver	Body	Viscera
Colour (Lovibond units) Y	11.5	10	9	2.0	15
(Lovibond units) R	3	10	0.5	0.5	2.8
Sp. gr. at 25°C........	0.8999	....	......	..	..
Ref. ind. at 25°C......	1.4750–1.4810	1.4753–1.4783	......	..	..
Iodine value.........	115.8–132.2	116.0–120.7	110–115	100	..
Acid value..........	1.2–2.0	15.0–17.4	......	..	..
Sap. value..........	170.4	168.3	168	195	..
Sat. fatty acids (%)...	18.5	....	11	..	..
Unsap. matter (%)...	5.0–8.6	7.7	3.7–5.8	0.7	..
Vit. A (B. U./g.).....	50,000–500,000	90,000–500,000	15,000–60,000	60	..
Vit. D (I. U./g.)......	1,000–6,000	1,000–5,000	600–1,000	..	..

The total production of ling-cod liver oil is utilized by the manufacturers of pharmaceutical products in their preparation of vitamin concentrates and medicinal oils.

(g) BLACK-COD OILS

The black cod, *Anoplopoma fimbria*, also known as the sablefish, coalfish and beshow, belongs to the family Anoplopomatidae. This fish weighs between 5 and 12 lb. and attains a length of 18 to 20 inches. It is a deep-water fish and may be found along the Pacific coast of America from Monterey to Unalaska, but it is more abundant in those regions frequented by the halibut, particularly on the off-shore banks of central and northern British Columbia. Black cod taken in southern waters are dry and tasteless, whilst those caught in the northerly waters are very rich in oil. The liver of the black cod is also very oily, some samples yielding as high as 30 per cent oil. The fish is caught throughout the year but the heaviest catch is taken between the months of June and October.

This fishery, of less importance than either the halibut or ling cod, has been fairly constant during the past few years with an average annual landing of 750,000 lb. In 1937 the landings increased to 1,341,000 lb. The catch is sold to the fresh, frozen, smoked and salted fish trades whilst the livers are saved for oil processing. There are no data available for the quantity of black-cod liver

oil now being produced, but, estimating from the quantity of black-cod livers landed in 1937, the approximate yield of liver oil would be 650 gallons.

Black-cod liver oil is a light yellow, clear liquid of relatively low and constant unsaturation. The percentage of unsaponifiable matter is also low for this type of oil and is similar to that of ling-cod liver oil. Table LXXX includes the analytical data obtained from numerous analyses made in these laboratories on this oil. The oil is used entirely for the manufacture of medicinal oils and vitamin concentrates.

The body oil of the black cod is of a light yellow colour and it deposits a large amount of stearine at room temperature [about 60 per cent of its volume at 18°C. (64.4°F.)]. It is not highly unsaturated, the iodine value averaging about 100. The oil contains but little unsaponifiable matter and gives only a slight colour with antimony trichloride. Some analytical data are given in the above table.

The oil yield from black-cod viscera (excluding liver and stomach) is slightly higher than that from halibut viscera, ranging from 4 to 10 per cent. It is a light yellowish-brown product with the same limits of unsaturation as the liver oil. The vitamin A potency is lower than that of halibut and ling-cod visceral oils but the vitamin D potency is about the same. Black-cod visceral oil is used for the manufacture of vitamin concentrates.

(h) RED-COD LIVER OIL

Of the numerous species of the family Scorpaenidae (rockfishes) found on the British Columbia coast, *Sebastodes ruberrimus*, *Sebastodes pinniger* and *Sebastodes introniger* are the species most commonly caught. These fish are bright vermilion in colour, weighing from 3 to 12 lb. and varying in length from 2 to 3 feet each. The three species differ from each other slightly in details of anatomical structure. The distribution of the species, which inhabit the deeper waters, extends from San Diego, California, to Alaska. Although these fish are generally known as red cod, rock cod, and red snapper, they are not related to the Gadidae or cod-fishes. Rockfishes are caught throughout the year but chiefly during the early spring and fall.

Red cod is fished commercially but is considered a minor fishery, the average yearly landings on the British Columbia coast being 213,400 lb., the greater part of which is sold on the fresh fish market. The market value is estimated to be about $9,000 annually.

The livers of the red cod are saved for the production of oil, and 11 cwt. was landed in British Columbia during 1937. Red-cod livers are small, forming 1 to 1.6 per cent of the total weight of the fish and ranging in oil content from 5 to 15 per cent. The oil from the fresh livers is clear and more highly pigmented than many of the fish liver oils produced on this coast. In table LXXX are a number of analytical values for red-cod liver oil. It is not highly unsaturated and the range is considerably less than that of halibut or ling-cod liver oils. The unsaponifiable matter is within the range of those found for halibut liver oil. Red-cod

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liver oil, like other fish oils of similar vitamin potency, is used in the production of medicinal oils and vitamin concentrates.

(i) SWORDFISH LIVER OIL

In the family of swordfishes, Xiphiidae, there is a single Canadian species. *Xiphias gladius*. This fish frequently attains a weight varying between 300 and 600 lb. and one of the outstanding physical characteristics is the long, strong snout, which is used as an effective weapon of attack. This swordfish is rather widely distributed and is taken on the Atlantic coast of America in considerable quantities (by means of harpoons) during the summer and early fall months, the peak of the catch occurring in July. The heaviest catches are taken off the east coast of Cape Breton.

TABLE LXXXI. Some chemical and physical properties of swordfish liver oil (Harrison *et al.* 1935)

Method of extraction	Ref. ind.	Iodine val.	Sap. val.	Unsap. (%)	F.A. as oleic acid	Vit. A (B.U./g.)
Petroleum ether...		135.9	148.8	14.7	26.2	
Petroleum ether...	.4821	154.8	166.9	11.8	33.2	
Ethyl ether.......	.4825	153.6	169.3	·10.9	28.1	86,000
Petroleum ether...	.4913	168.6	156.6	16.5	39.7	166,000
Boiling..........	.4747	137.1	183.5	3.3	23.9	13,500
Mechanical.......	.4740	137.8	181.9	3.6	31.0	20,000
Boiling..........	.4731	133.4	179.2	2.5	26.1	3,500
Boiling..........	1.4730	128.4	184.5	3.0	31.3	4,800
Boiling..........		147.0	182.4	3.4	46.1	

The swordfish industry is an old established fishery of Nova Scotia with an average yearly landing of 1,728,500 lb. for the years 1933 to 1937 inclusive. The entire catch is sold on the fresh fish market, whilst the livers are sold to various plants for oil processing. The method of preserving and shipping swordfish livers is similar to that used for the livers of the halibut. The average landing of livers is 22,100 lb. which would yield approximately 422 gallons of liver oil (solvent extraction).

The oil content of swordfish livers varies from 15 to 20 per cent, higher yields of oil being obtained from the livers of fish taken in the early fall. The liver oil is thick, viscous and of a reddish-yellow colour, with a musty odour. These characteristics are no doubt largely dependent upon the methods of extraction. An Atlantic coast swordfish liver oil prepared at the Atlantic Fisheries Experimental Station by solvent extraction and analysed in these laboratories gave 30 yellow and 9 red Lovibund units, refractive index of 1.4731 at 25°C., iodine value of 126.3, and acid value of 58.8. Further analyses on Atlantic coast swordfish liver oil are given in table LXXXI from the study of Harrison *et al.* (1935).

The data contained in this table show considerable variations in the physical

and chemical properties of this oil, as well as marked differences in some of the values in relation to the methods of extracting the oil. The variation in unsaturation may be partially attributed to the nature of the unsaponifiable material contained in the oil.

The marked difference between the amount of unsaponifiable material present in the ether-extracted and heat-extracted samples and the direct relationship of the unsaponifiable matter to the vitamin A potency are worthy of note. Samples of swordfish liver oil obtained at the peak of the fishing season, when tested biologically, proved to be 100 times as potent as the cod liver oil standard which contained 5,000 U.S.P. vitamin A units and 95 U.S.P. vitamin D units per gram.

The unusually high vitamin potency of swordfish liver oil makes it a valuable product, which is solely utilized in the manufacture of vitamin concentrates.

(j) HADDOCK LIVER OIL

One of the most popular and abundant of Atlantic coast sea fish is the haddock, *Melanogrammus aeglefinus*, which is a member of the family Gadidae. This fish averages about 3 lb. in weight and is procurable throughout the year, but is most plentiful from November to April. The flesh of the haddock is similar to that of the cod in quality. Practically the entire haddock catch is taken in Nova Scotia waters, whilst smaller catches are taken off Prince Edward Island and New Brunswick. The haddock fishery is one of the most important fisheries of the Atlantic coast and it has shown a general increase in the trend of landings since 1933 with the exception of 1937 when 38,806,800 lb. were landed as compared with 40,041,400 lb. in 1936. The greater percentage of the landed fish is sold fresh, whilst the remainder is smoked, green-salted, canned or dried.

The statistics pertaining to Atlantic fisheries do not include any data concerning the livers of the haddock, but these with other fish livers are processed for the oil they contain. The following information regarding haddock liver oil is taken from the paper of Pottinger *et al.* (1935) on Atlantic haddock liver oil. Oil obtained from fresh haddock livers is lighter than the average domestic cod liver oil, whilst the acid value is less than 2.8. Table LXXXII summarizes the analytical data obtained on this liver oil by the forementioned authors.

Haddock liver oil compared favourably with Atlantic cod liver oil in all chemical and physical properties with the exception of the iodine value, the former oil being more highly unsaturated than the latter. The unsaturation of haddock liver oil showed a seasonal as well as a locality variation. The majority of samples of this oil showed vitamin A and D potencies less than did the sample of cod liver oil used for comparison, but there appeared to be no definite seasonal trend.

As a medicinal oil, haddock liver oil would have to be blended with oil from cod livers to meet the standards of the U.S.P., but would no doubt prove an efficacious oil for animal and poultry feeding. Lower grades of this oil find use, as do the lower grades of cod oil, in the leather and tanning industries.

	Haddock	Hake	Genuine pollack	Cod, pollack, hake and cusk mixture
Sp. gr. at 25°C..............	0.9176–0.9239	......	......	.....
Colour (Lovibond units) yellow.	1.0–8.0	6–16	......	10
red....	0.0–1.2	0.8–2.3	......	30
Ref. ind. at 25°C.............	1.4769–1.4808	......	1.4788 (20°)	1.4762
Iodine value.................	156.8–181.2	134–158	155	168
Iodine value (chilled oil at 8°C.).	161.6–186.4	......	......	.....
Acid value...................	1.6–8.2	0.3–0.5	1	77
Sap. value...................	186.1–191.5	184–186	187	.....
Unsap. matter (%)...........	0.8–1.3	0.9–1.6	......	.....
Vit. A (B.U./g.)..............	100–310	......	......	.....
Vit. D (% of cod liver control)..	50–75	......	......	.....

(k) Hake Liver Oil

The Atlantic hake (*Urophycis* spp.) belongs to the family Gadidae. The closely related species of commercial importance are found from Newfoundland to Virginia. The fish are caught throughout the year but mainly during the summer months.

The hake fishery is one of the less important fisheries of the Atlantic coast. The catch is marketed in a variety of ways including fresh, canned, green-salted, smoked and dried. In New Brunswick, the livers of these fish are processed for their oil content, but the production has shown considerable variation during the past few years. In 1934, 22,815 gallons were produced, whilst for the years 1933, 1935 and 1936 the amount varied between 6,000 and 8,000 gallons, with a decided falling off in 1937 to 1,750 gallons. The statistics include the landings of this fish with those of cusk and it is not possible to state whether or not the fluctuation in oil production was due to the variable landings of fish.

The oil derived from the liver of the hake is yellow in colour and has a slightly lower and less extensive range of unsaturation than Atlantic cod liver oil. The content of unsaponifiable matter is approximately the same as cod liver oil. The vitamin A potency of this oil appears to be about the same as that of cod liver oil but the vitamin D potency is definitely less, in some cases containing not more than 10 per cent of that in a standard cod liver oil. However, a sample of oil from 50,000 kg. of hake liver examined by Bills *et al.* (1937) showed a vitamin A potency of 2,300 units per gram and a vitamin D potency of 130 units per gram. Some analytical data are given in table LXXXII.

Hake liver oil is blended with cod, pollack and cusk liver oils to produce a mixture suitable for animal nutrition, lower grades being used in the tanning and leather industries.

(l) POLLACK LIVER OIL

The pollack, *Pollachius virens*, also known as the coalfish or green cod, is a member of the family Gadidae and is common on both shores of the Atlantic ocean. It is taken in large quantities throughout the year in the western Atlantic on the fishing banks off the coasts of Nova Scotia and New Brunswick. The Canadian landings of this fish have shown a marked increase during the past few years, the landings for 1933 being 5,290,000 lb. and that for 1937 being 23,984,500 lb. The fish are marketed chiefly in the dried and green-salted state.

Pollack livers are utilized to a certain extent for their oil content, but the production figures show considerable annual variation. In 1935 New Brunswick produced 10,362 gallons, in 1936, 6,462 gallons and in 1937 only 2,275 gallons. Nova Scotia produced 2,000 gallons in 1936 and only 850 gallons in 1937.

Unfortunately we have not been able to obtain samples of pure pollack liver oil for analysis. Samples submitted to these laboratories have been mixtures of cod, pollack, hake and cusk liver oils. The analysis of one of such mixtures together with an analysis reported by Holmes (1924) for an unrefined sample of genuine pollack liver oil are given in table LXXXII. The mixed sample was prepared by sun-rotting and was of a very dark colour, possessing a high acidity and foul odour. The values reported by Holmes show that this oil is very similar in characteristics to cod liver oil. No extensive data appear to be available regarding the vitamin potency; Bills *et al.* (1937) report 2,800 units of vitamin A and 110 units of vitamin D in a sample of oil from 25,000 kg. of liver from fish taken off the coast of Maine.

TABLE LXXXIII. Characteristics of grayfish oils

	Liver (Pacific)	Liver (Atlantic)	Body (Pacific)
Sp. gr. at 25°C.	0.9055–0.9066	....	....
at 40°C.	0.8947	....	....
Viscosity at 25°C. (cps.)	48.4–49.2	....	....
at 40°C. (cps.)	32.4	....	....
Colour (Lovibond units) yellow	1.9–6.5	....	2.5
red		....	0.2
Optical activity (20 cm. at 25°C.)	−3.4°	....	....
Ref. ind. at 25°C. (αH)	1.4714	....	....
at 25°C. (DNa)	1.4702–1.4760	1.4753	1.4733
Iodine value	99.6–128.0	137.0	162.2
Acid value	0–0.57	0.16	....
Sap. value	152.1–164.9	....	167.5
Fatty acids (titre)	25.2	....	....
Acetyl value	5.5	....	....
Unsap. matter (%)	5.0–25.0	....	11.2
Vit. A (B.U./g.)	500–20,000	....	400–500
Vit. D (I.U./g.)	5–25	....	....

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(m) GRAYFISH OIL

The grayfish is a member of the Squalidae (the dogfishes), one of the largest and most primitive families of the Elasmobranchii (shark-like fishes). They are abundant in all cool seas. The Atlantic variety. *Squalus acanthias*, differs from the Pacific, *Squalus sucklii*, in that the former has shorter spines preceding the dorsal fin. In other respects they are similar. These small greedy sharks subsist on herring and other food fishes and are very destructive of fishermen's lines and nets. On the Pacific coast they may be caught throughout the whole year, but they are usually fished during the winter and spring months.

Grayfish oil has been produced on the British Columbia coast in considerable quantities during the past ten years, but it is only recently that the livers of these fish have been processed separately on a large scale. The statistics available list only the quantities of total oil produced from the whole fish. From 1933 to 1937 the Pacific coast production averaged about 140,000 gallons; from 1935 to 1937 the Atlantic coast production averaged about 10,000 gallons. During 1937, 180,000 lb. of grayfish livers were shipped from British Columbia to the United States for the production of a vitamin A oil for poultry purposes. This quantity of livers would produce about 11,000 gallons of oil.

The oil of the grayfish is stored mainly in the liver, the oil content of which varies from 40 to 70 per cent. The liver itself constitutes about 10 per cent of the weight of the whole fish. Pugsley (1939) observed that the oil content of the livers of the larger fish contained relatively less oil than those of the smaller fish and also that the percentage weight of the liver in the smaller fish was greater than that in the larger. In a large scale experiment where 8 tons of dogfish were put through a commercial reduction plant, 2028 lb. of livers were obtained from which 165 imperial gallons of oil were extracted. From the carcasses 63 gallons of body oil were obtained.

The oil can be extracted from the livers by simple steaming methods as discussed in Section 7. After the greater quantity of oil has been skimmed or drawn off the steamed mixture, the "chum" can be alkali-digested and a further yield of oil obtained. The body oil is usually produced by the continuous method of reduction or by methods involving the cooking and drying of the fish in open or vacuum cookers and the expression of the oil from the dried material by means of hydraulic presses. The oil obtained by the latter method is usually of a dark colour and high acidity. Some properties of the oils are given in table LXXXIII. The oil prepared from the strictly fresh livers is of a pale yellow colour with a slight fishy but not unpleasant odour. It contains but little stearine, and when freshly prepared remains fluid down to −5.6°C. (22°F.), after which it gradually becomes cloudy and semi-solid. There is a wide variation in unsaponifiable matter that so far has not been correlated with any other variable such as size of fish, sexual maturity, season, or locality. The examination of the unsaponifiable matter by E. G. V. Percival (unpub.) showed it to contain 5 per cent cholesterol, 85 per cent squalene and 10 per cent higher alcohols.

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Grayfish liver oil varies considerably in its content of yellow pigment and there is a distinct correlation between the intensity of this colour and the vitamin A potency. Red pigments are absent. Some of the larger fish possess livers with dark brown mottled patches whilst the others have the usual putty-coloured livers; the former produce oil with a deeper pigmentation and higher vitamin A potency than the latter.

The oil can be hydrogenated, but a preliminary refining either with alkali or with copper hydroxide is beneficial, as this oil, in common with most fish liver oils, contains traces of substances that inactivate the nickel catalyst. Such a refined oil, of iodine value 117 and melting point of $-10°C$. (14°F.), was hydrogenated to an iodine value of 51 when it had a melting point of 34.5°C. (94°F.). The product was odourless and tasteless, quite hard and almost pure white. Potassium and sodium soaps were hard and odourless and did not deteriorate noticeably on standing. They possessed fairly good lathering properties.

When grayfish liver oil is allowed to oxidize it becomes sticky and viscous, but does not form a solid film. Similarly, when heat-treated, this oil does not polymerize to any great extent. When a sample was heated to 250°C. (482°F.) in a vacuum for a period of 48 hours, the iodine value decreased from 108 to 80 and the viscosity rose from 0.6 to 0.96 poises at 25°C. Blowing heated air through the oil produces a greater effect; the oil darkens considerably and becomes quite viscous, but on exposure to the air the films still remain tacky. The hydroxylation and sulphonation of this oil have already been discussed in previous sections.

At the present time grayfish liver oil is being used as a blending oil in the preparation of poultry oils. It has also been used in the manufacture of blended medicinal oils (Thalattol) as a source of vitamin A. Both the liver and body oils can be used by the leather trades and also in insecticide sprays for codling-moth control and for tree banding. The body oil and lower grades of liver and mixed oils of the grayfish have been used in steel tempering and in the manufacture of sheep and cattle dips.

II. MISCELLANEOUS FISH OILS

In table LXXXIV are given some analytical data for a few oils that are not produced commercially in large quantities. Some of these are of theoretical interest only, but a few have been marketed in small amounts from time to time.

Anchovy Oil. The family Engraulididae is closely related to the Clupeidae but the fish are smaller, being about six or seven inches in length. Various species of Engraulididae exist in large schools and are found in all warm seas. Those taken in the more northerly waters have a rich oily flesh. The silver anchovy, *Anchovia browni*, abound in the sandy bays of Florida and as far south as Brazil, whilst the northern Pacific anchovy, *Engraulis mordax*, have a distribution ranging from lower California to the northern waters of British Columbia and Alaska.

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The anchovy is a valuable food fish but at the present time its use as such is comparatively small. Occasionally, large schools of these fish appear off the west coast of Vancouver island where they are taken by purse seiners. These fish are reduced to oil and fish meal. During the months of June, July and part of August, 1939, 1,800,000 lb. of anchovies were taken from the Barkley sound area on the west coast of Vancouver island. The yield of oil and meal from this quantity of fish was 12,080 gallons and 161 tons respectively.

As shown in table LXXXIV, the oil expressed from the anchovy is a clear, yellow liquid which is highly unsaturated. The percentage of unsaponifiable matter is low. The vitamin A potency for this particular body oil is slightly higher than that of pilchard and herring oils but the vitamin D content is lower. Anchovy oil is similar to pilchard oil in its behaviour towards oxidizing and polymerizing agents. Since it is produced only in small amounts, and because of its similarity to pilchard oil, it is usually mixed with the latter during commercial production.

TABLE LXXXIV. Miscellaneous oils

Kind	Refractive index	Iodine value	Acid value	Sap. value	Unsapon. matter (%)	Vitamin A (B.U./g.)	Vitamin D (I.U./g.)
Anchovy............	1.4789	171.2	0.5	187.1	0.5	100–200	5–25
Shark liver (B.C.)...	1.4744–1.4800	122–165	1.5–2.1	177	2.5–14.8	1,000–20,000	5–25
Shark liver (Pac.)...	1.4760–1.4924	135–329	0.1–1.5	22–183	1.9–89.2	1,000–100,000	.....
Ratfish liver (Pac.)..	....	86	....	145.5	22.2	100–500	0–5
Yellowtail (Atl)......	....	118	12.8	.....	.....	....	.....
Flounder liver (Pac.).	1.4892	152	7.7	.....	.....	10,000–30,000	1,000–2,000
Mackerel body (Atl).	1.4773	147	1.7	.....	.....	trace	.....
Albacore body (Pac.).	1.4860	198	0.2	186	.....	....	.....
Skate liver.........	1.4798	130–230	0.8–1.5	176–184	0.7–3.6	100–1,000	5–25
Eulachon body......	....	127	....	164	17.6	50	.....
Smelt viscera.......	1.4778	158	0.8	.....	.....	100–200	10–15
Perch liver.........	1.4751	131	3.6	.....	.....	....	.....
Sardine liver........	1.4815–1.4838	185–194	6–14	177–186	3.5–5.3	20,000–40,000	200–300

Shark liver oil is not regularly available. On the Pacific coast, a small quantity has been produced during the last few years chiefly as a source of vitamin A for poultry oil mixtures. The sharks most common in British Columbia waters, and which are usually taken for their oil, are the mud shark *Hexanchus griseus*, the sleeper shark *Somniosus microcephalus*, the basking shark *Cetorhinus maximus* and the blue shark *Prionace glauca*. The mud shark is the most common, and most of the shark liver oil produced has been from this species. The analytical data in table LXXXIV show a wide variation in unsaturation and unsaponifiable matter. In the latter, however, the range for the domestic oils is not so great as for those shark liver oils produced in more southerly waters, as the table shows. The most striking feature of these oils is the very high unsaponifiable range and the high degree of unsaturation. Oils with such values have not yet been reported from sharks taken in British Columbia waters.

Ratfish liver oil is not produced commercially in any great quantities. It is sometimes taken with grayfish and the mixture of the two reduced to meal and oil. The ratfish (*Hydrolagus colliei*) is common on the Pacific coast from California to Alaska. The livers are relatively large, ranging from 10 to 15 per cent of the weight of the whole fish. The oil content varies between 50 and 60 per cent. The liver oil deposits very little stearine but in spite of this is not very highly unsaturated. It clouds at −3°C. (26.6°F.) and solidifies at −12°C. (11.4°F.). The high content of unsaponifiable matter makes the hydrogenated oil of little value for food or soap-making purposes, but the raw or partially hydrogenated oil sulphonates well. The oil oxidizes very slowly and on this account has been found of some use in the lubrication of guns and fine machinery. In many places along the British Columbia coast fishermen and loggers use ratfish liver oil as a rubbing oil for muscular complaints. Indeed, with certain fishermen, the oil is regarded as an absolute necessity. This widespread use may have some scientific basis, as the unsaponifiable matter is said to be made up almost entirely of chimyl, batyl and selachyl alcohols which may facilitate absorption of the oil by the skin. The vitamin potency of ratfish liver oil is negligible.

Flounder liver oil is now being produced in small quantities as a source of the oil-soluble vitamins. On the Pacific coast there are a large number of flounders, all members of the Pleuronectidae. The oil is produced from the livers and viscera which are a by-product of a small fresh fish trade. On the Atlantic coast also there are several species taken commercially (e.g. Yellowtail). The samples at our disposal for analysis were too small for extensive examination but the oils seem to be of the same general nature as that of halibut liver oil. The vitamin potencies of the liver oil of the Pacific flounder also approximate that of halibut liver oil.

Mackerel oil has, as yet, not been produced in commercial quantities, the sample reported on in the above table being produced in a trial experiment to convert the waste from this fish into meal and oil. The landings of this fish on the Atlantic coast average about 21 million lb. per year, most of which is sold fresh. The flesh of this fish contains about 10 per cent oil, the nature of which approximates that of herring oil. The vitamin content is negligible.

Albacore oil is a by-product of the canning process. The albacore or long-finned tuna *Germo alalunga* is regularly caught off the coast of California but the fishery is becoming established in more northerly waters. During 1939 over 260,000 lb. of this fish were caught off the British Columbia coast. On the Atlantic coast the tuna or horse mackerel is landed in quantities averaging about 500,000 lb. annually. The body oil of this tuna is similar in properties to that of the albacore. Albacore oil is highly unsaturated, low in unsaponifiable matter and of light colour. According to Kniseley (1939) it can be used as a drying oil, and may, along with pilchard oil, successfully replace tung oil for certain purposes. The oil is not, as yet, a commercial product in Canada.

The liver oils of all the tunas are used for the manufacture of vitamin concentrates. However, we have failed to obtain genuine samples of these liver oils in sufficient quantities for analysis. Furthermore, enquiries amongst firms dealing

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in these products show that few, if any, chemical analyses are made, the only guarantee required being the vitamin potency.

Skate liver oil is not listed in the statistics as being produced commercially as a separate oil. The skates are members of the Rajidae, the most common on the British Columbia coast being the long-nosed skate *R. rhina*, the big skate *R. binoculata*, the prickly skate *R. stellulata* and the black skate *R. kincaidi*. Approximately 500,000 lb. a year of these fish are landed on the Atlantic coast but only about 80,000 lb. on the British Columbia coast. Of the former, the greater proportion is converted into fish meal and oil, but on the Pacific coast the only skate oil that is produced is from the few fish that are taken with grayfish and these go through the processing unsegregated. The analytical data for skate oil were taken from a paper by Tsujimoto (1936) and they show that this oil varies widely in unsaturation. Samples of domestic oils analyzed in these laboratories showed values midway between the limits given by Tsujimoto. In spite of the high unsaturation, skate liver oil does not possess any outstanding drying properties, films exposed to the air remaining thick and sticky for years. The oil sulphonates satisfactorily and can be used in leather manufacture. The vitamin potency is too low to warrant production as a poultry oil.

Eulachon oil is produced by the north Pacific coast Indians from the eulachon, *Thaleichthys pacificus*, a small fish related to the European smelt. The oil is highly prized by the natives and the fishery in the northern part of the province is reserved for them by the Government. A few thousand pounds are sold on the market, usually in the fresh or smoked condition. The oil is of no commercial importance, but in view of the large amounts consumed by the Indians a consideration of its properties is of some interest. It is of a light yellow colour and sets to a buttery solid when cooled to 10°C. (50°F.). If prepared from fresh fish, it has a not unpleasant odour and taste. The oil is not highly unsaturated and a slight amount of hydrogenation suffices to convert it into an odourless solid product. It possesses but little vitamin A or D, and in spite of the claims made for its medicinal properties, it must be concluded that its popularity amongst north Pacific coast Indians arises from the characteristic odour and taste occasioned by the primitive method of production, which allows of partial rotting of the fish prior to oil extraction. On account of the large quantities consumed, the oil can be looked upon as an important source of energy in the diet of these people.

The remainder of the oils included in the table are of no commercial interest. They are listed as a matter of record only.

III. OILS OF MARINE MAMMALS

Under this heading are included the whales, porpoises and belugas (white whales) belonging to the Cetacea, and the sea-lions and hair seals belonging to the Pinnipedia. The products from these animals landed in Canada during 1937 were worth $280,000 of which $223,000 was realized from the oils. Of this sizable industry whale oil represents the most important product, the value in 1937 being $197,227.

(a) OILS FROM CETACEANS

The cetaceans have a general similarity in body form to the fishes, but possess numerous anatomical characteristics that readily distinguish them from the latter. They are easily recognized by the horizontal flukes, and the fairly smooth skin, which in the case of the whales is very smooth and shiny. These marine mammals are warm-blooded and are able to maintain a constant temperature through having a fibrous layer immediately below the skin, which is loaded with oil and acts as an insulator. This fibrous layer is known as the blubber. Unlike the fishes, cetaceans obtain their supply of oxygen directly from the air taken in through the blow-hole.

The cetaceans are subdivided into two further groups, the Mystacoceti, and the Odontoceti. Porpoises and belugas belong to this latter group.

(i) WHALE OILS

These are obtained from a large number of different species of whales. Those taken in the north Pacific ocean are representative of the two large divisions mentioned above; Mystacoceti—those that possess whalebone, and Odontoceti—those that are provided with teeth instead of baleen. In the first division, the group known as rorquals or fin whales are the most common and these are particularly interesting, not only from an economic point of view, but also on account of the great size attained by certain species. These whales differ from the right whales in that they have much shorter, coarser and less flexible whalebone and long tapering flippers. The outstanding characteristic of all the rorquals is the long parallel grooves running longitudinally on the ventral surface. Included in this group of rorquals are the blue or sulphur-bottom whales, the finner whales or razorbacks, and the sei whales. The humpback whale is usually included in this group but is not considered a true rorqual. These whales have a world-wide distribution; they range in length from 30 to 100 feet and vary in weight from 50 to 120 tons. The females exceed the males in length by 1 or 2 feet.

The second division, the Odontoceti, includes the sperm whale, the bottlenose whale, the killer whales and the pilot whales. They are taken in all five oceans, but the sperm whale is the most valuable and the one taken most frequently in the north Pacific whaling area. This species of whale resembles a huge tadpole, in that the most massive and conspicuous part of the body is the head. In this part of the body is located the reservoir or "case" containing the valuable spermaceti oil. It is believed that this reservoir performs a hydrostatic function in the whale and it has been reported that as much as 15 barrels of spermaceti oil have been taken from one sperm whale. Sperm whales reach a length of between 30 and 60 feet, the female attaining a length of little more than half of that of the full-grown male. The blubber of this animal reaches a thickness of about 14 inches.

The whaling industry in Canada is mainly confined to the northern Pacific. There are two whaling stations located on the Queen Charlotte islands, equipped with a fleet of 7 killer boats. These stations have operated every year since 1920,

with the exception of 1921, 1931, 1932 and 1939. In table LXXXV is given a list of the various species taken from this area during the above period together with the quantities of oil produced. It is of interest to note the increasing percentage of sperm whales taken in the last four or five years. In 1936, 82 per cent of the whales caught were of this species. The proportion of sperm oil produced each year can be roughly estimated from the table, the actual production of this oil being 471,877 gallons in 1938. In relation to the world production of whale oil, the Canadian production is very small, the total world production for 1938-1939 being about 125 million gallons. This oil was produced from a catch of 38,321 whales of which but 3,000 were sperm whales. Over 85 per cent of the world's production of whale oil is made by the pelagic expeditions in the antarctic.

TABLE LXXXV. Number of whales landed and oil produced in British Columbia, 1922-1938

Year	Sperm	Sulphur-bottom	Fin	Hump-back	Sei	Right	Bottle-nose	Total	Oil (gal.)
1922...	38	4	94	50	1	.	.	187	283,314
1923...	94	62	166	78	53	.	2	455	706,514
1924...	83	56	125	47	100	2	1	414	645,657
1925...	76	29	135	40	68	.	3	351	556,939
1926...	80	14	124	25	25	1	.	269	468,206
1927...	82	10	138	21	7	.	.	258	437,967
1928...	83	47	140	21	13	.	1	305	571,914
1929...	146	16	168	9	67	.	1	407	712,597
1930...	147	10	62	12	89	.	.	320	525,533
1933...	190	1	17	..	1	.	.	209	509,310
1934...	265	..	71	14	..	.	.	350	813,724
1935...	175	6	20	1	..	.	.	202	426,772
1936...	311	3	48	14	2	.	.	378	763,740
1937...	265	1	44	7	..	.	.	317	662,355
1938...	252	4	50	4	..	.	.	310	539,077

The composition of whale oil has already been discussed in Section 2. In table LXXXVI will be found the range of analytical constants for a number of the more important whale oils of commerce. These data are taken largely from the work of Toyama and Uozaki (1937) and of Schweiger (1938). Due to modern methods of production the quality of the bulk of the whale oil now produced is very high. This is reflected in the low acid values given in the table. In the blubber oils the unsaponifiable matter rarely exceeds 3 per cent and there appear to be marked differences in the ranges of unsaturation, those of the sei whale and gray whale being the most unsaturated. As pointed out in Section 2, these blubber oils contain large proportions of monoethylenic acids of the oleic type. The qualities of the commercial oils, however, do not depend upon the unsaturation but on the colour and free-fatty-acid content.

The blubber and head oil of the bottlenose and sperm whales are characterized by large amounts of unsaponifiable matter, which consists largely of alcohols

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of high molecular weight (Section 3, page 88). Some analytical data on average samples of blubber and sperm whale oils produced on the British Columbia coast during 1938 are shown in table LXXXVII. These oils were of light colour, free from objectionable odour and of low free-fatty-acid content. They compared very favourably with the general quality of the oils produced by the pelagic expeditions during that year.

TABLE LXXXVI. Characteristics of oils from various species of whales

Species	Sp. gr. at .15 °C.	Acid val.	Iodine val.	Sap. val.	Unsap. mat. (%)	Unsat. F.A. (%)	Sat. F.A. (%)
Sei.	0.9196-0.9229	0.23-3.31	136.3-161.5	186.9-193.1	0.56-1.54	73.6-81.5	18.5-26.4
Fin.	0.9137-0.9236	0.44-1.43	107.4-155.8	190.3-196.5	0.32-1.98	25	75
Blue or Sulphur bottom	0.9140-0.9307	1	112.0-131.0	183.0-198.0	0.7 -3.5	73.7-86.4	13.6-26.3
Humpback...	0.9234-0.9154	0.36-0.81	120.3-159.4	183.5-190.1	0.31-0.64	87	13
Gray (Calif.)..	0.9290	0.5	147.0-167.0	191.0-193.0	1.6	83.8-90	10.0-14.2
Bottlenose ...	0.876-0.885	0.4 -1.8	79.7- 88.7	121.5-135.9	35.0-43.2		
Sperm.......	0.844-0.8808	1.0- 5.2	70.4- 96.4	120.0-150.3	17.5-44.0	81-90	10-19

TABLE LXXXVII. Characteristics of British Columbia whale oils

Oil	Acid val.	Iodine val.	Sap. val.	Unsap. mat. (%)	Sat. F.A. (%)	Colour Y.	Colour R.
Whale oil no. 1......	0.7	118	185	2.9	18.5	2.0	0.1
Sperm whale oil.....	0.5	76	135	30.1	11.6	1.0	0.1

Whale oils are utilized commercially chiefly in the hydrogenated form. Hydrogenated blubber oils are used in soaps and for the manufacture of margarines and shortenings. In Great Britain, between 80 and 90 thousand tons of whale oil were hydrogenated for margarine manufacture during 1937. In Germany, the consumption of whale oil for this purpose reaches about 180,000 tons annually. In other countries, more liberally supplied with dairy products, whale oil is hydrogenated chiefly for use in soaps, the annual consumption in the United States by this industry, for instance, being approximately 40,000 tons. In some countries, whale oil has been processed for use in the paint, varnish and linoleum industries, but the drying properties of even the most unsaturated whale oils are inferior to those of sardine and pilchard oils.

Bottlenose and sperm whale oils are more valuable than the blubber oils from the other species of whales. This is due chiefly to the content of unsatur-

ated alcohols which are now used as raw materials in the manufacture of many new types of detergents. One of the most important of these consists of sulphonated alcohols. These products are made in some cases by the sulphonation of alcohols resulting from the high-pressure hydrogenation of sperm oil. It is interesting to note that, whilst practically all of the Canadian whale oil is exported (over 80 per cent in 1937), Canadian firms who manufacture these new types of detergents have to import hydrogenated sperm oil and cetyl alcohol (a constituent of sperm oil) from foreign countries.

(ii) PORPOISE OILS

The family Delphinidae is included in the division Odontoceti, and embraces all porpoises and dolphins. The number of species in the Delphinidae is very large and only those that are common to the coastal waters of Canada will be described.

The common porpoise, *Phocaena phocaena*, occurs more abundantly than any other cetacean and is distinguished from other members of the Delphinidae by its small size, beakless head and triangular back fin. This species of porpoise is black on the back and white on the ventral surface. It rarely exceeds 6 feet in length. This species is widely distributed in the north Atlantic and ranges along the coast of America from Davis strait and the gulf of St. Lawrence to the coast of New Jersey. On the Pacific coast a closely related species, *Phocaena communis*, is common. It is similar in size and colour to the Atlantic species. The common dolphin, *Delphinus delphis*, has a very wide distribution in all temperate waters and is readily recognized by its well-defined narrow beak and distinctive colouring. It is black or dark brown on the back, and white on the ventral surface, whilst on each side there is an area of wavy bands or stripes of grey, yellow or white. The flippers and flukes are darkly pigmented. The dolphin does not as a rule attain a length of more than about 8 feet.

The porpoise is not taken for commercial purposes on the British Columbia coast. Although they are quite plentiful, they are widely scattered and rarely occur in schools of more than 6 to 8. They have to be captured by harpoons and in many trials the cost of hunting and processing the animals has not been warranted in view of the market value of the products. On the Atlantic coast they are landed chiefly for the oil contained in the blubber, head and jaw. The statistics show a considerable variation in the annual number of animals landed. In 1937 the catch is described as "beluga" or white whale, whilst for the previous years the catch is described as porpoises. The beluga, *Delphinapterus leucas*, is a true porpoise, but is to be distinguished from all other cetaceans by its whiteness and complete lack of any markings. These mammals are taken in Davis strait, Hudson bay and the gulf of St. Lawrence. The landings in 1937 are given as producing 19,120 gallons of oil.

A small Pacific coast porpoise was examined in these laboratories by Sunderland (1932). It was about 5 feet long and weighed 145 lb. The oils from the upper and lower jaws, skull and blubber, were expressed semi-quantitatively,

TABLE LXXXVIII. Characteristics of oils from the Pacific porpoise

Source	Upper jaw	Lower jaw	Skull	Blubber
Sp. gr. at 25°C..........	0.9360	0.9345	0.9186	0.9226
Ref. ind. at 25°C........	1.4529	1.4544	1.4650	1.4658
Iodine value............	32.7	36.7	74.3	89.3
Sap. value.............	312.0	298.7	221.1	230.2
Reichert-Meissl value....	136.0	130.9	19.6	33.9
Unsap. matter (%)......	1.0	1.1	1.5	0.6
Viscosity at 25°C. (poises)	0.46	0.50		0.51
Clouding point..........	−20°C.	−13°C.	3.0°C.	14°C.
Solidifying point........	−20°C.	−16°C.	−4.0°C.	−18°C.

when the following yields were obtained: upper jaw oil 3¼ oz., lower jaw oil 2½ oz., skull oil 1½ oz., and blubber oil 14 lb. These oils were analyzed with results shown in table LXXXVIII. As mentioned in Section 2, porpoise oils are peculiar in that they contain considerable proportions of iso-valeric acid and other fatty acids of low molecular weight. The valuable lubricating properties of these oils depend to a certain extent on the presence of these fatty acids, the amount of which is shown by the Reichert-Meissl values, high saponification values and low solidification points. From the above analyses it may be concluded that the oil from the upper jaw contains the largest proportion of acids of low molecular weight, with slightly less in oil from the lower jaw. The blubber oil contains more of these acids than that of the skull and in addition has a relatively low unsaturation. The blubber oil contains small amounts of vitamin A and some vitamin D.

TABLE LXXXIX. Characteristics of oils of the common dolphin (taken from glands at the articulation of the jaws, adipose tissue between the upper jaw and air-hole, tissue surrounding the skull, and blubber) and of the beluga or white whale.

Source	Dolphin				Beluga
	Glands	Adip. tiss.	Near skull	Blubber	
Sp. gr. at 15°C...........	0.9206	0.9308	0.9330	0.9285	0.9252–0.9290
Ref. ind. at 17°C.........	1.4548	1.4640	1.4790	....	1.4789–1.4738 (20°C.)
Iodine value............	17	56	133	129.7	92.8–128.3
Acid value..............	0.10	0.16	0.14	0.35	0.2–2.8
Sap. value	267	259	212	209.5	200.2–225.4
Unsap. matter (%).......	16.30	6.07	1.77	0.2	1.9
Reichert-Meissl value.....	145.3	111.3	39.1	32.8	16.7–35.3

Analyses of the oils from the common dolphin, *Delphinus delphis*, taken from the work of Marcelet (1926) and Klein and Stigol (1930), are given in table LXXXIX. In these animals, as in the porpoises, the glands of the jaw contain an oil that is rich in fatty acids of low molecular weight. In the sample reported in the above table the jaw oil contained an unusually high amount of

unsaponifiable matter, the corresponding oil from the porpoise containing only about 1 per cent of such material. The other characteristics of dolphin oil are similar to those of the porpoise oils.

Some analyses of the blubber oils of the beluga or white whale have been reported by Belopol'skii and Maksimov (1934), the data for which are shown in table LXXXIX. From these analyses it is evident that this blubber oil has much the same properties as those of the porpoise and dolphin.

The jaw oils of these mammals have been used for a long time for the lubrication of fine mechanisms such as watches, scientific instruments and the like. The blubber oil has been used to a certain extent as a lubricant for high-speed spindles and for the prevention of rust in such articles as guns, knives and other metallic implements. Other minor uses of this blubber oil are in leather dressing, the tanning of certain kinds of leathers and the preparation of chamois.

(b) SEAL OILS

The true seals, fur seal and sea-lions are members of the group of Carnivora known as Pinnipedia. They are aquatic and have in some respects a fish-like form, yet possess many characteristics of terrestrial animals. The limbs are to a considerable extent enclosed within the skin of the trunk. The hands and feet are fully webbed, the latter being fused to the tail. The seals that are captured commercially belong to two families, the Phocidae and the Otariidae. The first family includes eight species, which are known as true seals. They are differentiated from other families in that they have no external ears and the hind limbs are completely fused to the tail. The Otariidae are less modified; the external ear is present and the hind limbs are not of such little use on land. The fur seal is a member of this family as also is the sea-lion which is the largest member of the group, some individuals attaining a length of 13 feet. The various species of hair seals and sea-lions are widely distributed, particularly in the colder waters of the northern and southern Pacific and Atlantic oceans and the polar regions. They are captured chiefly for their hides and blubber oil. Those landed in Canada are taken mainly on the Labrador coast and in the gulf of St. Lawrence. On the British Columbia coast, hair seals are a menace to the fishing industry, causing considerable damage to fishing gear and destroying large numbers of salmon. During recent years a bounty has been paid for their destruction, but the number captured has not, up to the present, warranted their utilization in oil manufacture. The annual production of seal oil on the Atlantic coast has shown a marked increase since 1933. The yield of oil for that year was 7,630 gallons and for each successive year a decided increase has been shown, reaching a maximum in 1937 of 75,699 gallons.

Seal and sea-lion blubber oils have much the same properties as whale blubber oils. They are not very highly unsaturated and have a large content of monoethylenic fatty acids. Consequently, these oils do not possess any drying properties but, on absorbing oxygen, become thick and sticky. They have been used as adulterants for cheap paints, but their use for this purpose should be discouraged.

TABLE XC. Characteristics of blubber oils from hair seals and sea-lions

	Harbour seal	Greenland seal	Steller's sea-lion
Ref. ind. at 25°C.	1.4742	1.4776	1.4731–1.4737
Iodine value...............	141.8	127–162	123–130
Sap. value.................	189.9	178–196	185–187
Sat. fatty acids (%)	10.6	....	15–17
Stearin (%)..............	3.0	....	2.8–4.8
Unsap. matter (%).........	1.4	....	1.4–1.5
Vit. A (B.U./g.)	45	....	250–350
Vit. D (I.U./g.)	25	....	35

There is but little difference between the properties of sea-lion blubber oil and those of seal oil, and for most purposes both of them can replace whale oil in commercial usage. They have been used for the manufacture of certain types of soft soaps, for the preparation of chamois by the French method and also in the compounding of lubricants. When hydrogenated, the hardened product can be used for the same purposes as those from hardened fish and whale oils. The vitamin potencies of these blubber oils are too low to warrant their utilization as animal feeding or medicinal oils.

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SECTION 11. CHANGES IN THE OILS OF FISHERIES PRODUCTS

The tendency of fish oils to undergo oxidative changes, as discussed in Section 6 of this Bulletin, naturally raises the question of the effect of these substances on the stability of food products containing them. The present Section is an attempt to summarize our knowledge concerning this subject with particular reference to frozen fish, salted, smoked and dried fish, canned fish, and finally, fish meals. No attempt is made here to evaluate the food value of the oils in fisheries commodities except where changes in the oil may show an effect on the nutritional value of such commodities.

I. EDIBLE PRODUCTS

(a) FROZEN FISH.

The changes in the oil of cold-stored fish may conveniently be discussed under three headings, hydrolysis, rancidity and "rusting". It will be subsequently apparent that these effects are sometimes intimately related.

(i) HYDROLYSIS

In Section 6 attention was drawn to the action of fat-splitting enzymes, the lipases, and it was shown how, immediately after death of an organism, the tissue-lipases cause an increase in the free fatty acids of the oil. It was further pointed out that, although the low temperatures employed for the cold-storage of fish greatly retarded the action of the lipases, the development of free fatty acids was still significant, particularly in fish stored for extended periods.

Early workers in the field (Smith 1913; Perlzweig and Gies 1913) could not detect any changes in the oil of fish cold-stored for periods up to two years. Later, however, Clark and Almy (1920) found that the free fatty acids in cold-stored fish did actually increase but, probably owing to their methods of extraction, no relation to time or conditions of storage was proven. Ono (1935) showed that the lipases in fish tissue were active at $-13°C$. and that they caused considerable increase in the free fatty acids of the oils of fish stored at this temperature.

In 1933 the writer reported some results of an investigation on the hydrolysis of the oil in cold-stored salmon. The data concerned (1) the acidity of the oil of salmon stored in a commercial cold-storage for various lengths of time, (2) the acidity of the oil in glazed and unglazed salmon stored at different temperatures, and (3) the effect of storing in various gases. The data showing the development of acidity in commercially-stored salmon has been discussed in Section 6 (table XXVIII). It might be remarked that some salmon held in commercial cold-storage for a period of two years at an average temperature of $-13°C$. yielded oils that were 45 per cent hydrolyzed.

The data given in table XCI show that glazing has practically no effect on the rate of hydrolysis of the oil in cold-stored salmon and that small differences in storage temperatures, i.e. from $-11.6°$ to $-13.8°C.$, had no significant effect. The data show conclusively that the acidity of the oil in the deep pink muscle undergoes more extensive hydrolysis than that of the superficial dark muscle. A gradation in acidity is also noticeable within the deep pink muscle itself.

Storage of salmon at −13°C. in oxygen or carbon dioxide had no noticeable effect on the hydrolysis of the oil, practically the same values being obtained for fish so stored as for those in the ordinary atmosphere of the cold rooms. There was also no significant difference between fish stored in the "round" and those that had been eviscerated. It was thought that, in the fish stored in the "round", the enzymes from the viscera might possibly penetrate into the muscle tissue prior to freezing, but the data do not support this idea. Storage of fish in ammonia, as would be expected, considerably reduced the amount of free fatty acids in the oil of both the pink and the dark muscle. Judging by the emulsion formed whilst extracting these oils, it appears that the low free-fatty-acid content of the oil was due to partial neutralization of the fatty acids and not to the inhibition of the lipase activity by ammonia. It was interesting to observe that the free fatty acids were partially neutralized even in the inner pink muscle, thus indicating the extent of the penetration of the ammonia gas.

TABLE XCI. Effect of temperature and glazing on hydrolysis of salmon (red spring) oil

Condition of fish	Time in storage (months)	Temperature of storage			Acid value of oil from	
		Low (°C.)	High (°C.)	Average (°C.)	Pink muscle	Dark muscle
Glazed...	7	−14	−7	−11.6	11.6	6.8
Unglazed.	7	−14	−7	−11.6	11.3	6.6
Glazed...	12	−14	−7	−11.6	12.4	8.8
Unglazed.	12	−14	−7	−11.6	14.8	7.0
Glazed...	7	−16	−11	−12.5	11.2	7.6
Unglazed.	7	−16	−11	−12.5	14.2	6.6
Glazed...	12	−16	−11	−12.5	12.5	9.9
Unglazed.	12	−16	−11	−12.5	12.7	7.5
Glazed.		−16	−11	−13.8	9.6	6.4
Glazed...	12	−16	−11	−13.8	14.4	12.6
Unglazed.	12	−16	−11	−13.8	10.2	6.7
Glazed...	3	−29	−1		10.2	5.6
Unglazed.	3	−29	−1		7.6	3.7
					Inner Outer	
Glazed...		−29	−1		14.3 10.8	8.4
Unglazed.		−29	−1		21.4 14.1	8.9
Glazed...	12	−29	−1		14.3	11.3
Unglazed.	12	−29	−1		14.5	11.3

The development of a small amount of free fatty acids in the oil of fisheries food products is probably in itself not very serious. Barnicoat (1931) investigated the effect of non-oxidized free fatty acids on the flavour of beef, fat and lard containing from a trace to as much as 15 per cent free fatty acids. When tasted hot (60°C.), none of the samples containing free fatty acids could be consistently

differentiated from its neutral control. If anything, samples containing from 3 to 5 per cent of free fatty acids were preferred to the bland, insipid, neutral controls. When tasted cold, no harsh effects were noticed, but a curious effect was observed in the harder beef and mutton kidney fats in that a sensation of filming over the tongue and palate was experienced even in the presence of 1 per cent free fatty acids. This effect was not increased by increase in free fatty acids, was much less marked in the case of softer lower-melting-point fats (in which classification fish oils would be included) and was practically destroyed by the presence of other food in the mouth. Free fatty acids in cold-stored fish may, however, become objectionable if such fish are baked or fried. According to Gwynn and Lee (1931) the smoking point of a fat decreases almost logarithmically with the fatty acid content "which means that the first small increment in a nearly neutral fat is as objectionable as a great increment in a fat of high free fatty acid". The smoking of a fat indicates decomposition, and the products have a sharp acrid odour and taste.

The relationship between free-fatty-acid development and rancidity in oils and in the "rusting" of cold-stored fish, is not at all clear. Oils containing free fatty acids are not necessarily rancid, but rancid oils usually contain some free fatty acids. As indicated later, there is possibly some connection between free fatty acids and the deterioration known as "rusting".

(ii) RANCIDITY

The great susceptibility of fish oils to atmospheric oxidation and the occurrence of oxidative enzymes in fish muscle make cold-stored fatty fish very liable to rancidification. Very low temperatures and heavy ice glazes are the chief means of avoiding such changes. The most valuable studies in this field have been made by Banks and Lea of the Food Investigation Board of Great Britain. The following is a brief summary of their work to date.

Lea (1932) drew attention to the fact that the edible period of chilled beef is usually limited by the spoilage of the fat, which spoilage is due to a taint produced by micro-organisms and only to a slight extent by atmospheric oxidation. Storage of beef in atmospheres containing 20 per cent or more of carbon dioxide considerably decreased tainting by inhibiting the growth of micro-organisms. In the same report, Coyne (1933) reported that the use of carbon dioxide on chilled fish had a beneficial effect on their keeping qualities. So far, no work has been reported on the effect of carbon dioxide on frozen fatty fish.

In the report for 1935, Banks discussed the rancidity of fat in cold-stored herring and showed that brine-frozen herring stored at −20°C. gave definite signs of rancidity after a three-months' storage period, whereas air-frozen herring were free from rancidity after six-months' storage at this temperature. Banks further emphasized the fact that glazing is of great importance, more particularly in brine-frozen fish, since most of the brine is washed off during the glazing. Brine-frozen, glazed herring were free from rancidity after six-months' storage at −28°C. Low temperatures, absence of brine and good glazing were, therefore, indicated for the prevention of rancidity in stored herring.

In a related investigation Lea (1936) reported on the effects of temperature and traces of metals on the oxidation of herring oil. The results showed "that a decided advantage is to be gained by the use of very low temperatures, peroxide values after 90 and 180 days at 0°, −10°, and −20°C. being 37.0, 14.5 and 5.5; and 71.0, 28.0 and 10.5 ml. (of 0.002 N. thiosulphate) per gram." The presence of one part of copper in ten million parts of a solution in contact with the oil increases the rate of oxidation 2.5 times. Iron present in ten times the quantity was only half so effective whilst sodium chloride actually retarded oxidation. Further investigation by Banks (1938) revealed that the apparent pro-oxidative activity of common salt is due to the activation of an enzyme system present in fish muscle tissue. This enzyme system is capable of oxidizing fats at −20°C. and is considerably activated by the presence of small amounts of sodium chloride.

Later work by Banks (1938, 1939) was concerned with the effect of temperature and time of storage on the potency and activation of this muscle enzyme system. Extremely interesting results have been obtained. In the first place extracts from the muscle of fresh drift-net herrings caught in the summer were found to be about three times as potent as that of autumn-caught, fresh, trawled herring. Banks clearly differentiates between the potency and activity of the enzyme system present in muscle tissue. Although no data have as yet been published by this investigator, it is assumed that the activity will be smaller the lower the temperature. The potency of muscle tissue extracts is, however, affected in a peculiar manner. If extracts are stored at −10°C., the potency of the enzyme system (tested by measuring the increase in peroxide content of herring oil at −2.5°C.) gradually decreases. If the extracts are stored at −20°C., however, there is a marked *increase* in potency up to about 64 days, after which the potency drops to approximately that of the fresh tissue extract. At −30°C. the same effect was found except that the maximum potency was developed after only 27 days at this lower temperature.

Banks therefore concludes that there are at least two factors of importance in connection with the storage of herring (and presumably of other fatty fish), first the activity of the oxidizing enzyme at the temperature of storage, and second the change in potency (or concentration) at that temperature. He suggests that a short period of storage at −10°C. "might prove a beneficial prelude to storage at lower temperatures". Finally, sodium chloride increases the activity of the enzyme system and any circumstance that tends to increase the concentration of this salt in the tissue will result in increased activity of the oxidizing enzyme system.

(iii) RUSTING

A type of deterioration that is particularly prevalent in cold-stored fatty fish is the appearance of a reddish brown scum. Dependent upon storage conditions, this "rusting" may make its appearance within three to six months after storage. It appears first on the napes or other exposed cut surfaces, as a rule beginning at the oily layer just under the skin. Thence it spreads over the white

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surface of the belly of the fish and finally over the entire surface of the body. Rusting appears to be a surface phenomenon and is more marked in poorly glazed fish or where the glaze has become cracked or evaporated. This rust may spread below the surface of the glaze, but in some cases may be found on the outer surface. Rusted fish usually have a rancid flavour when cooked.

Early work seemed to indicate that this discoloration was entirely an oxidation process. Dutch workers (Meded. Nederl. Vereenig. Koeltechniek, 1925) summarize their work on this phenomenon as follows: the action of the oxygen of the air on the fat (of fish) causes oxidation and a brown discoloration. This discoloration is facilitated by an easy access of air to the fat caused by insufficient ice glaze, too high a temperature of storage and the penetration of certain salts into the flesh of the fish. Iron salts are particularly effective in producing a brown discoloration. Elimination or lessening of the effect was obtained by packing fish in vacuum tins in nitrogen or by freezing and storing fish in blocks of ice. Paper-lined boxes improved the product but did not entirely eliminate rusting. These workers could not decide whether or not hydrolysis of the oil had any relation to the amount of rusting.

Brocklesby and Denstedt (1932) investigated the rusting of cold-stored salmon and found that the acid value of the oil of rusted fish is no criterion of the degree of rusting, although in every case the oil from rusted fish contained free fatty acids. The manner in which the oil and rust was isolated from the rusty fish was found to be important. The oil, extracted by heating with water and pressing, did not give a peroxide test and contained but a trace of nitrogen. On the other hand, solvent-extracted oils gave intense peroxide tests, contained large amounts of nitrogen and, in addition, were thick and gummy. Careful mechanical isolation of the rust showed that it, too, contained considerable amounts of nitrogen, and, although some ammoniacal soaps were present, most of the nitrogen was associated with non-hydrolyzed oil. Later work showed that an atmosphere of ammonia hastened the appearance and increased the severity of rusting. Perfectly fresh salmon oils, when spread on diatomaceous earth and exposed to an atmosphere containing ammonia, appeared to oxidize much more quickly than oils similarly exposed in ammonia-free atmospheres. In the presence of ammonia, the oxidized product was reddish-brown in colour and appeared very similar to the rust isolated from stored salmon.

Halibut contains but little oil, but sometimes suffers rusting during prolonged cold-storage. The writer examined 50 halibut that had been held in cold-storage until they were no longer saleable. These were arranged in increasing degree of rusting as indicated by visual inspection. The glaze was then tested with an indicator and it was found that there was a definite relationship to the alkalinity of the melting glaze and the degree of rusting. The more alkaline the glaze the greater was rusting. The alkalinity of the glaze was due to ammonia or ammonia-like substances.

Carrying this work further, Bedford (1934) considered that bacterial action on fish muscle might produce ammoniacal substances that would give a rusty

colour with fish oils. The characteristic red colour was obtained in halibut body or halibut head oil by the volatile bases produced by the micro-organisms from bilge-water, acting on raw halibut muscle juice, boiled halibut broth, gelatine or peptone as a source of nitrogen. With peptone the colour was produced more quickly than with the other nitrogenous substances. Bedford observed that the reacting substance from the nitrogen source is slowly volatile at 25°C. and rapidly at 100°C. One of the volatile substances produced is ammonia, but the colour it produced when used alone had not the same intensity of redness as that caused by the volatile products from the bacterial medium. Since an increase of peptone also increased the rate of colour formation, Bedford concluded that fresh fish, that have not been well preserved before freezing, and which therefore have an increased peptone content due to bacterial action, will be more susceptible to subsequent rusting in cold storage than fish which have not been subjected to bacterial decomposition.

In this connection the work of Davies and Gill (1936) is of some interest. These workers state that with increasing fishiness (flavour) of fish oils and ether extracts of fish products the total nitrogen and organic nitrogen content increase. Nitrogen can enter into combination with unsaturated oils when kept for a period of weeks in contact with a source of nitrogen such as casein, betaine or lecithin. Trimethylamine oxide reacts with such oils to develop a fishy odour. Davies and Gill also observed that the colour of cod liver oil darkens progressively with the amount of combined nitrogen. They suggest that the oxidation of unsaturated fats in the presence of nitrogenous substances leads to progressive darkening.

Whether or not free fatty acids have any influence on the formation of rust, is as yet not definitely known. The creeping of the rust over the surface of the fish and sometimes over the outer layer of the glaze may, however, be related to the free-fatty-acid content of the oil.

(b) Dried, Salted and Smoked Fish

Whilst it is well known in the industry that oily dried and salted fish have a pronounced tendency to go rancid, very few investigations have been reported on the subject. In regard to the preservation of Atlantic mackerel, the United States Bureau of Fisheries investigated the development of rancidity, which form of deterioration is very serious with this fish. Working with a highly smoked frozen product Stansby (1935) was able to show that the development of rancid flavour was more or less correlated with the increase in peroxide content of the oil. In unfrozen iced fish, protein changes mask the development of rancid flavour, but there is a definite increase in peroxide content of the oil, the increase being greater in eviscerated than in whole fish. Fresh mackerel are usually shipped by floating them in water-tight barrels containing sea-water and ice, a practice that leads to the rapid decomposition of the fish. Peroxide values of the oil in "floated" fish develops more slowly than those of iced fish but the formation of free fatty acids is more rapid in fish treated by the former method than in those treated with ice alone.

Lemon, Stansby and Swift (1937) claim that the use of oat flour improves the quality of salted mackerel. Two interesting statements are made by these authors. The first is that the use of salt greatly increases the efficiency of the oat-flour treatment, a statement that is surprising in view of the accelerating action of salt on the oxidizing enzymes present in fish muscle. Secondly, these investigators claim that the peroxide value of the oil could not be used as a means of determining rancidity, and recourse to organoleptic tests had to be made. Based on these tests it was concluded that oat flour (30 per cent of the weight of salt used) exerted a favourable influence on the keeping qualities of salt mackerel when used during the preliminary salting treatment. It was found advisable to omit the oat flour, when re-packing the fish. It may be recalled that Lowen, Anderson and Harrison (1937) investigated the effectiveness of oat flour as an antioxidant for fisheries products, and, whilst showing that some retardation of rancidity could be attributed to the flour, its effect was much smaller in fisheries products than in fatty vegetable or lard products. These authors also ran into difficulty with the peroxide test as a measure of rancidity. It seems possible, therefore, that atmospheric oxidation, in the absence of an enzyme system, might take place under such conditions that peroxides break down so rapidly that they cannot be used as a measure of rancidity.

In respect to the use of cereal flours as antioxidants for fisheries products the Quaker Oat Company has issued a series of instructions for the use of oat flour (Avenex) in the processing of canned sardines; smoked, cured and spiced herring; fresh and frozen mackerel, salmon and halibut; and salt mackerel. These applications are covered by numerous patents held by S. Musher, a few of which are as follows. According to U.S. patent 2,029,248 the surface of meat, fish, etc., is dusted with an antioxidant material such as pulverized oats, which may be mixed with salt. The antioxidant may also be incorporated into the surface of wrapping paper, etc. U.S. patent 2,176,022 stipulates the use of unbleached cereal flour such as oats and degerminated maize or barley. The use of finely divided de-oiled seed residues such as soy bean flour is mentionedi n U.S. patent 2,176,024. The stabilization of meat and fishery products with an aqueous or alcoholic extract of unbleached oat or corn flour is protected by U.S. patent 2,176,028. It is claimed that these cereal and seed products are suitable for use on fresh and frozen fillets and also for dried and salted products.

Rapoport-Roitman and Ozetskii (1938) have shown that the fat of salted fish stored at 18° to 20°C. gradually increases in acid value; when this value reaches 20 the fish are definitely rancid. To prevent such rancidity in salted fish, Bahr and Wille in British patent 386,482 suggest the use of small amounts of certain phenols such as hydroquinone, eugenol or alpha-naphthol. The salted fish may be packed in brine containing the antioxidant or the latter may be added to the salt used for curing. J. A. S. van Deurs in British patent 303,059 prefers to surround the fish with materials having a pH less than 5, which, he claims, protects the fish from rancidity.

The smoking of oily fish is claimed to make them more stable to oxidative

changes. According to Takahashi and Masuda (1938) strong antioxidative properties are acquired by the fish, probably owing to the phenols contained in the smoke. The oxygen absorption of smoked fish oil, as indicated by the formation of peroxides and the Kreis reaction, was strongly inhibited in contrast to the unsmoked oil. The vitamin A content of smoked fish is but slightly affected by smoking, the effect being proportional to the surface exposed and the duration of heating prior to the smoking operation.

(c) CANNED FISH

In considering the oil in canned fish, it is natural to deal separately with (1) those cases in which, during the canning of sardines, herring, tuna and similar fish, a vegetable oil is added to the fish before canning and certain changes take place when the vegetable oil mixes with the natural oil of the fish, and (2) those cases in which the natural oil of the canned fish is a primary index of quality and (as for canned salmon) the amount and colour of the free oil is used as one of the criteria in grading the pack.

According to Lepierre and de Carvalho (1932) the vegetable oil used in canning fish loses its characteristics because of the diffusion of the fish oil into the vegetable oil, even during the early stages of processing. This diffusion depends upon the process used for canning, the quality of the fish, the time of year when the fish are caught and the length of time elapsing between canning and opening of the tin. Miyama and Saruya (1934) packed a number of vegetable oils in cans, sterilized them and allowed them to stand for two years. During that time there was no change in the iodine value or acid value of the oils. When, however, these same oils were mixed with tuna fish, canned and allowed to stand for two years, the acid value of the free oil was found to have doubled. This was interpreted to mean that an increase in acid value had actually taken place during the storing of the sterilized tins. According to the writer's experience, however, this is not necessarily true. During the exhaust-box treatment given canned salmon the heat penetration is not sufficient to inactivate all enzymes, with the result that the oil from the centre of the steak of fish almost invariably has a higher acid value than the free oil on the outside. In the case of added vegetable oil, the acidity would gradually increase as the high acid oil from the interior of the steak gradually mixed with that from the outside. The sterilization process should be adequate to inactivate all enzymes and it is probable that the so-called "ripening" of canned tuna packed in oil is a physical rather than an enzymatic process.

The retorting or sterilization process effects an increase in the oil of canned fish. In the case of salmon Brocklesby (1933) found that the acid value of the oil of red springs sterilized in glass jars at 117°C. increased at the rate of 0.09 per hour whilst the oil from coho sterilized in tins under the same conditions increased 0.23 per hour. It was suggested that the acid value of the oil of canned salmon might be used as an index of quality, since incipient hydrolysis before canning is very much greater than that brought about by the sterilization process. Subse-

quent data, however, obtained by the Canned Salmon Inspection Laboratories, Vancouver, B.C., would indicate that the correlation between acid values of the oil and other criteria of quality is very low.

The volume of free oil in canned salmon is one of the chief criteria by which quality is judged. Charnley (1936, 1937) gives some interesting data regarding the oil content of Canadian canned salmon. Arranged in descending order of average free-oil content in samples of 12 cans, the different species of salmon follow the order spring, sockeye, coho, pink, blueback (immature coho) and chum. The relative variation in free-oil content is greatest in the last species. In British Columbia canned sockeye salmon there is considerable seasonal variation in the amount of free oil, the maximum amount being obtained during the latter part of July and the first part of August. Comparison of British Columbia canned sockeye with that of Alaska-caught fish shows that the "average free oil in British Columbia sockeye falls in the 'better-than-average' interval for Alaska Red salmon". Finally, Charnley observes that the popular idea that the free-oil content of canned salmon increases for a considerable time after packing is probably erroneous. The time elapsing between the date of packing and that of inspection has only a negligible effect on the free-oil content of the canned product.

Owing to the fact that nearly all the oxygen is exhausted during processing and that sterilization temperatures inactivate the enzyme systems present in fish flesh, little change in the characteristics of the oil of canned fish is to be expected. In the examination of many samples of oil from canned salmon of all species made in these laboratories no indications of rancidity have ever been obtained.

II. FISH MEALS

Fish meal is a valuable product of the fish "reduction" plant. It is manufactured from small fish such as herring and pilchard, from the refuse of large fish used for human consumption such as salmon and halibut, and from fish not used by man for food. Fish meal is used principally as an animal foodstuff. Commercial meals may be classified as non-oily and oily, the former containing up to two per cent and the latter up to six per cent.

The oil content is of value in the preparation of a balanced diet in animal feeding. It is apparently not detrimental to the digestibility of the proteins of the meal. DeWildt (1929a) found that fish meal extracted with the fat-solvent trichlorethylene was not as effective as the non-extracted meal in increasing the weight of pigs. However, this solvent removed not only fatty material but also some of the proteins and de Wildt (1929b) suggested that both factors were instrumental in changing the food value of the meal. Oya and Matida (1938) found that the protein of a sardine meal of inferior quality containing 5 per cent of ether-extractable material was equal in digestibility to the ether-extracted meal when tested *in vivo* and superior when tested *in vitro*. Bömer *et al.* (1935)

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reported that pigs showed a greater increase in weight when fed an oily herring meal than when fed a less oily herring meal.

The development of rancidity in an oil exposed to the air has been discussed in detail in Section 6. It is necessary here only to point out that conditions conducive to preservation of the oil in a fish meal are poor because of the large surface exposed to the air. Hydrolysis of the oil in herring meal was demonstrated by Moen (1933). Fresh meal contained some 5 per cent free fatty acids, whereas old samples contained up to 40 per cent. Moen claimed that the amount of free fatty acids in herring meal could be used, in addition to other criteria, in the determination of its age, although this was not substantiated by Günther (1931), nor by Oshima and Sugawara (1936). However, Takano (1937) showed that the acid value of the ether extract increased with the oxidation of the meal, particularly when the meal was moist, free fatty acids increasing to 15 per cent in 100 days. Schmalfuss et al. (1933) showed that some fish meals became acid on storage and also that unsaturated fatty acids were converted into hydroxy acids.

Harrison (1939) has shown that the amount of solvent-extractable material in a fish meal varies with the solvent used, being lowest with the hydrocarbons and highest with dioxane. Of great importance is the fact that the solvent-extractable material decreases with all common solvents during oxidation of the oil in the meal, the decrease in Harrison's experiments varying from 3 to 67 per cent. This had been shown by Oshima et al. (1936) when ether was used as solvent. The decrease was due to the oxidation of the fatty acids into ether-insoluble materials, most of which were soluble in acetone and could be made soluble in ether by heating the oxidized meal with 20 per cent hydrochloric acid before extraction. The diminution in yield of extract, according to Takano (1937) is due to oxidation of the more highly unsaturated fatty acids of the oil, followed by polymerization into less soluble materials.

Apart from the mechanical effect of increasing the surface of the oil exposed to the air, fish meal may cause changes in the oil in other ways. Banks has shown that herring muscle contains a fat-oxidizing enzyme system which is activated by sodium chloride. Like other enzyme systems, however, it is inactivated by heat and is presumably destroyed during the cooking of the meal. Oya and Nonaka (1938) have shown that fish oils adsorbed on sardine meal and other proteins for 30 days and then removed by extraction with ether are definitely darkened by contact with the proteins. Adsorption on non-protein material does not give the same darkening.

Deterioration of the oil in fish meal results in a decreased food value of the meal. Bömer et al. (1935) have shown that meal stored for one to two years loses some of its efficiency in the fattening of pigs. It is well known that vitamin A is destroyed by rancid fat, and the use of cereal flours in fish meals might be worth investigating from the standpoint of their antioxidative action. Although vitamin D is more stable than vitamin A towards oxidation, there is some evidence that it too is destroyed when the oil of a fish meal becomes rancid. Carver et al.

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(1937) found that vitamin D, sufficient in amount in a fresh salmon meal to protect chicks against rickets when the meal formed 2.9 per cent of the diet, was insufficient in meal one year old, when fed at the same level. The same proportion of meal, mixed with the rest of the ration and then stored one year, was adequate. This suggests that the cereal portion of the ration contained antioxidants sufficient to protect the vitamin D.

Oily fish meals, improperly stacked during storage, will heat up in the interior of the stack owing to oxidation of the oil, and the meal will become darkened and develop a scorched taste. R. W. Harrison (private communication) has followed the development of heat in fish meals by thermocouples and will shortly have some interesting and valuable suggestions to make regarding the methods of packaging such meals. In an effort to overcome surface oxidation of the oil in herring and sardine meal some firms have resorted to packaging the meal in the form of small briquets. The fresh meal is exposed to high pressures to form solid compact lumps of low air-permeability and small surface area. Tests made on these briquets indicate that the loss of vitamins during storage is definitely less than in the ordinary, finely divided, sacked meal.

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